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(54) Title: CURABLE PHOTOCHROMIC COMPOSITIONS INCLUDING (METH)ACRYLATE, AMINE, AND ISOCYANATE FUNCTIONAL COMPONENTS

(57) Abstract: The present invention relates to, a curable photochromic composition that includes: (a) a photochromic compound; (b) a (meth)acrylate functional component including at least one (meth)acrylate group, and having a (meth)acrylate equivalent weight of 500 g/mole to 10,000 g/mole; (c) a polyamine component including at least two amine groups, wherein each amine group is independently selected from primary amine and secondary amine, provided the polyamine component includes at least two primary amine groups, and wherein the polyamine component has an amine equivalent weight of 30 g/mole to 250 g/mole; and (d) a polyisocyanate component including at least two isocyanate groups, and having an isocyanate equivalent weight of less than or equal to 500 g/mole, wherein each isocyanate group of the polyisocyanate component is reversibly blocked with a blocking agent. The curable photochromic composition optionally includes (e) a catalyst. The present invention also relates to an article that includes: a substrate; and a photochromic layer over at least one surface of the substrate, where the photochromic layer is formed from the curable photochromic composition of the present invention.

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CURABLE PHOTOCHROMIC COMPOSITIONS INCLUDING (METH)ACRYLATE, AMINE, AND ISOCYANATE FUNCTIONAL COMPONENTS

FIELD

[001] The present invention relates to curable photochromic compositions, which include, a photochromic compound, a (meth)acrylate functional component, a polyamine component, a polyisocyanate component, and optionally a catalyst.

BACKGROUND

[002] In response to certain wavelengths of electromagnetic radiation (or "actinic radiation"), photochromic compounds, such as indeno-fused naphthopyrans, typically undergo a transformation from one form or state to another form, with each form having a characteristic or distinguishable absorption spectrum associated therewith. Typically, upon exposure to actinic radiation, many photochromic compounds are transformed from a closed-form, which corresponds to an unactivated (or bleached, e.g., substantially colorless) state of the photochromic compound, to an open-form, which corresponds to an activated (or colored) state of the photochromic compound. In the absence of exposure to actinic radiation, such photochromic compounds are reversibly transformed from the activated (or colored) state, back to the unactivated (or bleached) state. Compositions and articles, such as optical lenses, that contain photochromic compounds or have photochromic compounds applied thereto (e.g., in form of a photochromic coating composition) typically display colorless (e.g., clear) and colored states that correspond to the colorless and colored states of the photochromic compounds contained therein or applied thereto.

[003] Photochromic compounds can be used in curable compositions to form, for example, cured layers, such as cured films or sheets that are photochromic. With cured photochromic films, such as cured photochromic coatings, it is typically desirable that they provide a combination of hardness and photochromic performance. Generally, the kinetics associated with the reversible transformation of a photochromic compound between a closed-form (unactivated / colorless) and an open-form (activated / colored) is faster in a soft matrix, but slower in a hard matrix (of the cured film in which the photochromic compound resides). Cured photochromic films having a soft matrix typically have reduced hardness, while those having a hard matrix typically have increased hardness.

[004] It would be desirable to develop curable photochromic compositions that provide cured photochromic layers having a desirable level of hardness without a reduction in photochromic performance.

SUMMARY

[005] In accordance with the present invention, there is provided a curable photochromic composition comprising: (a) a photochromic compound; (b) a (meth)acrylate functional component comprising at least one (meth)acrylate group, and having a (meth)acrylate equivalent weight of 500 g/mole to 10,000 g/mole; (c) a polyamine component comprising at least two amine groups, wherein each amine group is independently selected from primary amine and secondary amine, provided the polyamine component comprises at least two primary amine groups, and wherein the polyamine component has an amine equivalent weight of 30 g/mole to 250 g/mole; (d) a polyisocyanate component comprising at least two isocyanate groups, and having an isocyanate equivalent weight of less than or equal to 500 g/mole, wherein each isocyanate group of the polyisocyanate component is reversibly blocked with a blocking agent; and (e) optionally a catalyst.

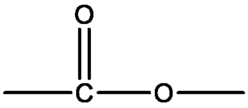
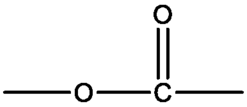
[006] In accordance with the present invention, there is further provided an article comprising: (A) a substrate; and (B) a photochromic layer over at least one surface of the substrate, wherein the photochromic layer is formed from the curable photochromic composition of the present invention, as described above and further herein.

[007] The features that characterize the present invention are pointed out with particularity in the claims, which are annexed to and form a part of this disclosure. These and other features of the invention, its operating advantages and the specific objects obtained by its use will be more fully understood from the following detailed description in which non-limiting embodiments of the invention are illustrated and described.

DETAILED DESCRIPTION

[008] As used herein, the articles "a," "an," and "the" include plural referents unless otherwise expressly and unequivocally limited to one referent.

[009] Unless otherwise indicated, all ranges or ratios disclosed herein are to be understood to encompass any and all subranges or subratios subsumed therein. For example, a stated range or ratio of "1 to 10" should be considered to include any and all subranges between (and inclusive of) the minimum value of 1 and the maximum value of 10; that is, all subranges or subratios beginning with a minimum value of 1 or more and ending with a maximum value of 10 or less, such as but not limited to, 1 to 6.1, 3.5 to 7.8, and 5.5 to 10.

[010] As used herein, unless otherwise indicated, left-to-right representations of linking groups, such as divalent linking groups, are inclusive of other appropriate orientations, such as, but not limited to, right-to-left orientations. For purposes of non-limiting illustration, the left-to-right representation of the divalent linking group  $-\overset{\overset{\large O}{\|}}{C}-O-$ or equivalently -C(O)O-, is inclusive of the right-to-left representation thereof,  $-O-\overset{\overset{\large O}{\|}}{C}-$, or equivalently -O(O)C- or -OC(O)-.

[011] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification and claims are to be understood as modified in all instances by the term “about.”

[012] As used herein, molecular weight values of polymers, such as weight average molecular weights (Mw) and number average molecular weights (Mn), are determined by gel permeation chromatography using appropriate standards, such as polystyrene standards. Average molecular weights of(meth)acrylate functional components, according to some embodiments of the present invention, such as those prepared in the examples herein, can be determined by ^{1}H NMR.

[013] As used herein, the term “polymer” means homopolymers (e.g., prepared from a single monomer species), copolymers (e.g., prepared from at least two monomer species), and graft polymers.

[014] As used herein, the term “(meth)acrylate” and similar terms, such as “(meth)acrylic acid ester” means methacrylates and/or acrylates. As used herein, the term “(meth)acrylic acid” means methacrylic acid and/or acrylic acid.

[015] As used herein, the term “photochromic” and similar terms, such as “photochromic compound” means having an absorption spectrum for at least visible radiation that varies in response to absorption of at least actinic radiation. Further, as used herein the term “photochromic material” means any substance that is adapted to display photochromic properties (such as, adapted to have an absorption spectrum for at least visible radiation that varies in response to absorption of at least actinic radiation) and which includes at least one photochromic compound.

[016] As used herein, the term “actinic radiation” means electromagnetic radiation that is capable of causing a response in a material, such as, but not limited to, transforming a photochromic material from one form or state to another as will be discussed in further detail herein.

[017] As used herein, the term “photochromic material” includes thermally reversible photochromic materials and compounds and non-thermally reversible photochromic materials and compounds. The term “thermally reversible photochromic compounds/materials” as used herein means compounds/materials capable of converting from a first state, for example a “clear state,” to a second state, for example a “colored state,” in response to actinic radiation, and reverting back to the first state in response to thermal energy. The term “non-thermally reversible photochromic compounds/materials” as used herein means compounds/materials capable of converting from a first state, for example a “clear state,” to a second state, for example a “colored state,” in response to actinic radiation, and reverting back to the first state in response to actinic radiation of substantially the same wavelength(s) as the absorption(s) of the colored state (e.g., discontinuing exposure to such actinic radiation).

[018] As used herein to modify the term “state,” the terms “first” and “second” are not intended to refer to any particular order or chronology, but instead refer to two different conditions or properties. For purposes of non-limiting illustration, the first state and the second state of a photochromic compound can differ with respect to at least one optical property, such as but not limited to the absorption of visible and/or UV radiation. Thus, according to various non-limiting embodiments disclosed herein, the photochromic compounds of the present invention can have a different absorption spectrum in each of the first and second state. For example, while not limiting herein, a photochromic compound of the present invention can be clear in the first state and colored in the second state. Alternatively, a photochromic compound of the present invention can have a first color in the first state and a second color in the second state.

[019] As used herein the term “optical” means pertaining to or associated with light and/or vision. For example, according to various non-limiting embodiments disclosed herein, the optical article or element or device can be chosen from ophthalmic articles, elements and devices, display articles, elements and devices, windows, mirrors, and active and passive liquid crystal cell articles, elements and devices.

[020] As used herein the term “ophthalmic” means pertaining to or associated with the eye and vision. Non-limiting examples of ophthalmic articles or elements include corrective and non-corrective lenses, including single vision or multi-vision lenses, which can be either segmented or non-segmented multi-vision lenses (such as, but not limited to, bifocal lenses, trifocal lenses and progressive lenses), as well as other elements used to correct, protect, or enhance (cosmetically or otherwise) vision, including without limitation, contact lenses, intra-ocular lenses, magnifying lenses, and protective lenses or visors.

[021] As used herein the term “display” means the visible or machine-readable representation of information in words, numbers, symbols, designs or drawings. Non-limiting examples of display elements include screens, monitors, and security elements, such as security marks.

[022] As used herein the term “window” means an aperture adapted to permit the transmission of radiation there-through. Non-limiting examples of windows include automotive and aircraft transparencies, windshields, filters, shutters, and optical switches.

[023] As used herein the term “mirror” means a surface that specularly reflects a large fraction of incident light.

[024] As used herein the term “liquid crystal cell” refers to a structure containing a liquid crystal material that is capable of being ordered. A non-limiting example of a liquid crystal cell element is a liquid crystal display.

[025] As used herein, spatial or directional terms, such as "left," "right," "inner," "outer," "above", "below," and the like, relate to the invention as described further herein, in accordance with some embociments. It is to be understood, however, that the invention can assume various alternative orientations and, accordingly, such terms are not to be considered as limiting.

[026] As used herein, the terms "formed over,” "deposited over," "provided over," “applied over,” residing over,” or “positioned over,” mean formed, deposited, provided, applied, residing, or positioned on but not necessarily in direct (or abutting) contact with the underlying element, or surface of the underlying element. For example, a layer "positioned over" a substrate does not preclude the presence of one or more other layers, coatings, or films of the same or different composition located between the positioned or formed layer and the substrate.

[027] All documents, such as but not limited to issued patents and patent applications, referred to herein, and unless otherwise indicated, are to be considered to be "incorporated by reference" in their entirety.

[028] As used herein, the term “aliphatic” group(s) means groups that include single bonds, double bonds, and/or triple bonds, and which are not aromatic as described in further detail herein. The term “aliphatic” group(s), as used herein, also includes linear or branched aliphatic groups and cycloaliphatic groups.

[029] As used herein, recitations of “linear or branched” groups, such as linear or branched alkyl, are herein understood to include: a methylene group or a methyl group;

groups that are linear, such as linear C_2-C_{20} alkyl groups; and groups that are appropriately branched, such as branched C_3-C_{20} alkyl groups.

[030] The term "alkyl" as used herein means linear or branched C_1-C_{25} alkyl. Linear or branched alkyl can include C_1-C_{25} alkyl, such as C_1-C_{20} alkyl, such as C_2-C_{10} alkyl, such as C_1-C_{12} alkyl, such as C_1-C_6 alkyl. Examples of alkyl groups from which the various alkyl groups of the present invention can be selected from, include, but are not limited to, those recited further herein.

[031] The term "cycloalkyl" as used herein means groups that are appropriately cyclic, such as, but not limited to, C_3-C_{12} cycloalkyl (including, but not limited to, cyclic C_3-C_{10} alkyl, or cyclic C_5-C_7 alkyl) groups. Examples of cycloalkyl groups include, but are not limited to, those recited further herein. The term "cycloalkyl" as used herein also includes: bridged ring polycycloalkyl groups (or bridged ring polycyclic alkyl groups), such as, but not limited to, bicyclo[2.2.1]heptyl (or norbornyl) and bicyclo[2.2.2]octyl; and fused ring polycycloalkyl groups (or fused ring polycyclic alkyl groups), such as, but not limited to, octahydro-1H-indenyl, and decahydronaphthalenyl.

[032] The term "heterocycloalkyl" as used herein means groups that are appropriately cyclic, such as, but not limited to, C_2-C_{12} heterocycloalkyl groups, such as C_2-C_{10} heterocycloalkyl groups, such as C_5-C_7 heterocycloalkyl groups, and which have at least one hetero atom in the cyclic ring, such as, but not limited to, O, S, N, P, and combinations thereof. Examples of heterocycloalkyl groups include, but are not limited to, imidazolyl, tetrahydrofuranyl, tetrahydropyranyl and piperidinyl. The term "heterocycloalkyl" as used herein also includes: bridged ring polycyclic heterocycloalkyl groups, such as, but not limited to, 7-oxabicyclo[2.2.1]heptanyl; and fused ring polycyclic heterocycloalkyl groups, such as, but not limited to, octahydrocyclopenta[b]pyranyl, and octahydro-1H-isochromenyl.

[033] The descriptions, classes, and examples provided herein with regard to alkyl groups, cycloalkyl groups, heterocycloalkyl groups, haloalkyl groups, and the like, are also applicable to alkane groups, cycloalkane groups, heterocycloalkane groups, haloalkane groups, etc., such as, but not limited to, polyvalent alkane groups, such as polyvalent alkane linking groups, such as divalent alkane linking groups.

[034] As used herein, the term “aryl” and related terms, such as “aryl group”, means an aromatic cyclic monovalent hydrocarbon radical. As used herein, the term “aromatic” and related terms, such as “aromatic group,” means a cyclic conjugated hydrocarbon having stability (due to delocalization of pi-electrons) that is significantly greater than that of a hypothetical localized structure. Examples of aryl groups include C_6-C_{14} aryl groups, such as, but not limited to, phenyl, naphthyl, phenanthryl, and anthracenyl.

[035] The term “heteroaryl”, as used herein, includes, but is not limited to, C_3-C_{18} heteroaryl, such as, but not limited to, C_3-C_{10} heteroaryl (including fused ring polycyclic heteroaryl groups) and means an aryl group having at least one hetero atom in the aromatic ring, or in at least one aromatic ring in the case of a fused ring polycyclic heteroaryl group. Examples of heteroaryl groups include, but are not limited to, furanyl, pyranyl, pyridinyl, quinolinyl, isoquinolinyl, and pyrimidinyl.

[036] Representative alkyl groups include, but are not limited to, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, neopentyl, hexyl, heptyl, octyl, nonyl and decyl. Representative cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cyclooctyl.

[037] As used herein, the term “halo” and related terms, such as “halo group,” “halo substituent,” “halogen group,” and “halogen substituent,” means a single bonded halogen group, such as -F, -Cl, -Br, and -I.

[038] As used herein, recitations of “halo substituted” and related terms (such as, but not limited to, haloalkyl groups, haloaryl groups, and halo-heteroaryl groups) means a group in which at least one, and up to and including all of the available hydrogen groups thereof is substituted with a halo group, such as, but not limited to F, Cl or Br. The term “halo-substituted” is inclusive of “perhalo-substituted.”

[039] As used herein, “at least one of” is synonymous with “one or more of,” whether the elements are listed conjunctively or disjunctively. For example, the phrases “at least one of A, B, and C” and “at least one of A, B, or C” each mean any one of A, B, or C, or any combination of any two or more of A, B, or C. For example, A alone; or B alone; or C alone; or A and B; or A and C; or B and C; or all of A, B, and C.

[040] As used herein, “selected from” is synonymous with “chosen from” whether the elements are listed conjunctively or disjunctively. Further, the phrases “selected from A, B, and C” and “selected from A, B, or C” each mean any one of A, B, or C, or any combination of any two or more of A, B, or C. For example, A alone; or B alone; or C alone; or A and B; or A and C; or B and C; or all of A, B, and C.

[041] The curable photochromic compositions of the present invention include a (meth)acrylate functional component that includes at least one (meth)acrylate group, and having a (meth)acrylate equivalent weight of 500 g/mole to 10,000 g/mole. With some embodiments, the (meth)acrylate functional component includes 1 to 10 (meth)acrylate groups, or 1 to 8 (meth)acrylate groups, or 1 to 6 (meth)acrylate groups, or 1 to 5 (meth)acrylate groups, or 1 to 4 (meth)acrylate groups. With some embodiments, the (meth)acrylate functional component includes at least one methacrylate group, or at least one acrylate group, or combinations of methacrylate groups and acrylate groups. In accordance with some embodiments, the (meth)acrylate functional component includes at least one acrylate group, and is free of methacrylate groups, in which case the (meth)acrylate functional component can be referred to as an acrylate functional component. In accordance with some further embodiments, the (meth)acrylate functional component includes at least one methacrylate group, and is free of acrylate groups, in which case the (meth)acrylate functional component can be referred to as a methacrylate functional component.

[042] The (meth)acrylate functional component, with some embodiments, has an average molecular weight of 1000 g/mole to 10,000 g/mole, or from 1200 g/mole to 8000 g/mole, or from 1500 g/mole to 5000 g/mole.

[043] With some embodiments, the (meth)acrylate functional component is present in an amount of from 10 percent by weight to 50 percent by weight, or from 15 percent by weight to 40 percent by weight, or from 20 percent by weight to 35 percent by weight, the percent weights in each case being based on total resin solids weight of the curable photochromic composition.

[044] In accordance with some embodiments, the (meth)acrylate functional component includes: (i) a first (meth)acrylate functional component having one (meth)acrylate group; and optionally (ii) a second(meth)acrylate functional component having at least two (meth)acrylate groups. The first (meth)acrylate functional component having one (meth)acrylate group, with some embodiments, has: a (meth)acrylate equivalent weight of 1000 g/mole to 10,000 g/mole; and an average molecular weight of 1000 g/mole to 10,000 g/mole. The second (meth)acrylate functional component having at least two (meth)acrylate groups, with some embodiments, has: a (meth)acrylate equivalent weight of 500 g/mole to 5000 g/mole; and an average molecular weight of 1000 g/mole to 10,000 g/mole.

[045] With some embodiments, the second (meth)acrylate functional component having at least two (meth)acrylate groups, when present, has 2 to 10 (meth)acrylate groups, or 2 to 8 (meth)acrylate groups, or 2 to 6 (meth)acrylate groups, or 2 to 5 (meth)acrylate groups, or 2 to 4 (meth)acrylate groups.

[046] In accordance with some embodiments, when the composition includes both first and second (meth)acrylate functional components, the first (meth)acrylate functional component having one (meth)acrylate group is present in an amount of from 10 percent by weight to 50 percent by weight, or from 15 percent by weight to 40 percent by weight, or from 20 percent by weight to 35 percent by weight, the percent weights in each case being based on total resin solids weight of the curable photochromic composition. The second (meth)acrylate functional component having at least two (meth)acrylate groups, when present, with some embodiments, is present in an amount of from 1 percent by weight to 30 percent by weight, or from 5 percent by weight to 25 percent by weight, or from 10 percent by weight to 25 percent by weight, the percent weights in each case being based on total resin solids weight of the curable photochromic composition.

[047] The (meth)acrylate functional component, with some embodiments, includes at least one of a polyether, a polyester, a polycarbonate, and/or a polyurethane, which in each case includes at least one (meth)acrylate group. With some embodiments, the (meth)acrylate functional component includes at least one of an aliphatic polyether, an aliphatic polyester, an aliphatic polycarbonate, and/or an aliphatic polyurethane, which in each case includes at least one (meth)acrylate group. The (meth)acrylate functional polyether, polyester, polycarbonate, and polyurethane components, in each case, independently have (meth)acrylate equivalent weights and ranges, and average molecular weights and ranges as recited previously herein with regard to the (meth)acrylate functional component.

[048] The polyester having at least one (meth)acrylate group includes a plurality of carboxylic acid ester linkages (-C(O)-O-). With some embodiments, the polyester having at least one (meth)acrylate group is an aliphatic polyester. With some embodiments, the polyester includes a linear or branched C_2-C_{20} alkyl linkage and/or a C_3-C_{10} cycloalkyl linkage, independently between and/or extending from each carboxylic acid ester linkage. The polyester having at least one (meth)acrylate group can be prepared in accordance with art recognized methods. With some embodiments, and for purposes of non-limiting illustration, a hydroxyl functional (meth)acrylate, such as 4-hydroxybutyl acrylate and/or 4-hydroxybutyl methacrylate, is reacted with a cyclic ester, such as ε-caprolactone, which results in the formation of a (meth)acrylate functional polyester.

[049] The polyether having at least one(meth)acrylate group includes a plurality of ether linkages (-O-). With some embodiments, the polyether is an aliphatic polyether. With some embodiments, the polyether includes a linear or branched C_2-C_{20} alkyl linkage and/or a C_3-C_{10} cycloalkyl linkage, independently between and/or extending from each ether linkage. The polyether having at least one(meth)acrylate group can be prepared in accordance with art recognized methods. With some embodiments, a polyether having at least one hydroxyl group is reacted with acrylic acid and/or methacrylic acid, which results in the formation of a (meth)acrylate functional polyether.

[050] The polycarbonate having at least one(meth)acrylate group includes a plurality of carbonate linkages (-O-C(O)-O-). With some embodiments, the polycarbonate is an aliphatic polycarbonate. The polycarbonate, with some embodiments, includes a linear or branched C_2-C_{20} alkyl linkage and/or a C_3-C_{10} cycloalkyl linkage, independently between and/or extending from each carbonate linkage. The polycarbonate having at least one (meth)acrylate group can be prepared in accordance with art recognized methods. With some embodiments, a polycarbonate having at least one hydroxyl group is reacted with acrylic acid and/or methacrylic acid, which results in the formation of a (meth)acrylate functional polycarbonate.

[051] The polyurethane having at least one (meth)acrylate group includes a plurality of urethane linkages (-O-C(O)-N(H)-). The polyurethane having at least one (meth)acrylate group, with some embodiments, is an aliphatic polyurethane. With some embodiments, the polyurethane includes a linear or branched C_1-C_{20} alkyl linkage and/or a C_3-C_{10} cycloalkyl linkage, independently between and/or extending from each urethane linkage. The polyurethane having at least one (meth)acrylate group can be prepared in accordance with art recognized methods. With some embodiments, a polyurethane having at least one hydroxyl group is reacted with acrylic acid and/or methacrylic acid, which results in the formation of a (meth)acrylate functional polyurethane.

[052] Examples of commercially available (meth)acrylate functional materials that are useful as (or as part of) the (meth)acrylate functional component include, but are not limited to: (meth)acrylate terminated poly(L-lactide) having a molecular weight of 2500 g/mole; and poly(ethylene glycol) methyl ether (meth)acrylates having a molecular weight range of from 1000 to 5000 g/mole, which are commercially available from Millipore Sigma.

[053] As used herein, and with regard to the curable photochromic composition, the term “total weight of resin solids” and similar terms, such as “total resin solids weight” and “total resin solids” means the total weight of the (meth)acrylate functional component, the polyamine component, and the polyisocyanate component, and unless otherwise stated, does not include the weight of the photochromic compound(s) and other optional additives, such as catalyst.

[054] The curable photochromic compositions of the present invention include a polyamine component that includes at least two amine groups. Each amine group of the polyamine component is independently selected from primary amine and secondary amine, provided the polyamine component includes at least two primary amine groups.

[055] With some embodiments, the polyamine component has a Mw of from 100 g/mole to 2500 g/mole, or from 100 g/mole to 2000 g/mole, or from 100 g/mole to 1500 g/mole.

[056] In accordance with some embodiments, the polyamine component includes at least one amine group that is blocked with an aldehyde group or a ketone group.

Reaction or blocking of a primary amine of the polyamine with an aldehyde or ketone results in the formation of an imine. Reaction or blocking of a secondary amine of the polyamine with an aldehyde or a ketone results in the formation of an enamine. In accordance with some further embodiments, the polyamine component includes at least one primary amine group that is blocked with an aldehyde group or a ketone group, examples of which include, but are not limited to: methyl isobutyl ketone (MIBK); methyl ethyl ketone (MEK); acetone; acetaldehyde; ethylaceto acetate; and methyl propyl ketone (MPK).

[057] The polyamine component has an amine equivalent weight of from 30 g/mole to 250 g/mole, or from 40 g/mole to 200 g/mole, or from 50 g/mole to 150 g/mole. The recited amine group equivalent weight values, and related ranges, of the polyamine component, in each case represent a combination (or sum) of primary amine group equivalent weight, secondary amine equivalent weight, and blocked amine group equivalent weight.

[058] The polyamine component, with some embodiments, is present in the curable photochromic composition in an amount of from 2 percent by weight to 12 percent by weight, or from 3 percent by weight to 11 percent by weight, or from 4 percent by weight to 10 percent by weight, the percent weights in each case being based on total resin solids weight of the curable photochromic composition.

[059] The reaction or blocking of a primary amine group, of the polyamine component, with an aldehyde or ketone results in the formation of an imine group. In accordance with some further embodiments, and not intending to be bound by any theory, it is believed that one or more imine groups of the polyamine component de-block, resulting in the formation of a primary amine that reacts with an isocyanate group of the polyisocyanate component, and aldehyde and/or ketone that volatilizes out of the composition.

[060] The polyamine component, with some embodiments, includes at least one of aliphatic polyether, aliphatic polyester, aliphatic polycarbonate, polyethylenimine, or aliphatic polyurethane, each independently having at least two amine groups, where each amine group is independently selected from primary amine and secondary amine, provided the polyamine component includes at least two primary amine groups. The amine functional aliphatic polyether, amine functional aliphatic polyester, amine functional aliphatic polycarbonate, polyethylenimine, and amine functional aliphatic polyurethane (which each independently have at least two amine groups), in each case, independently have amine equivalent weights and ranges, and Mw values and ranges as recited previously herein with regard to the polyamine component.

[061] The aliphatic polyether having at least two amine groups includes a plurality of ether linkages (-O-). With some embodiments, the aliphatic polyether, having at least two amine groups, includes a linear or branched C_2-C_{20} alkyl linkage and/or a C_3-C_{10} cycloalkyl linkage, independently between and/or extending from each ether linkage. The aliphatic polyether having at least two amine groups can be prepared in accordance with art recognized methods. With some embodiments, a hydroxyl functional polyether having at least two hydroxyl groups is reacted with an aziridine, which results in the formation of an amine functional polyether intermediate having at least two primary amine groups. Non-limiting examples of commercially available amine functional aliphatic polyethers include JEFFAMINE® polyether amines (from Huntsman Corporation). In accordance with some embodiments, at least one amine, such as a primary amine, of the aliphatic polyether having at least two amine groups, can be blocked with an aldehyde group or a ketone group.

[062] The aliphatic polyester having at least two amine groups includes a plurality of carboxylic acid ester linkages (-C(O)-O-). With some embodiments, the aliphatic polyester, having at least two amine groups, includes a linear or branched C_2-C_{20} alkyl linkage and/or a C_3-C_{10} cycloalkyl linkage, independently between and/or extending from each carboxylic acid ester linkage. The aliphatic polyester having at least two amine groups can be prepared in accordance with art recognized methods. With some embodiments, a polyester having at least two hydroxyl groups is reacted with an aziridine, which results in the formation of an amine functional polyester having at least two primary amine groups. In accordance with some further embodiments, a hydroxyl terminated aliphatic polyester, in a first step undergoes a condensation reaction with N-benzyloxycarbonyl amino acid, followed by catalytic hydrogenation, in a second step, which results in the formation of a primary amine functional aliphatic polyester, such as described in Bioconjugate Chemistry, 2002, 13(5), pp 1159-1162. In accordance with some embodiments, at least one amine, such as a primary amine, of the aliphatic polyester having at least two amine groups, can be blocked with an aldehyde group or a ketone group.

[063] The aliphatic polycarbonate having at least two amine groups includes a plurality of carbonate linkages (-O-C(O)-O-). With some embodiments, the aliphatic polycarbonate, having at least two amine groups, includes a linear or branched C_2-C_{20} alkyl linkage and/or a C_3-C_{10} cycloalkyl linkage, independently between and/or extending from each carbonate linkage. The aliphatic polycarbonate having at least two amine groups can be prepared in accordance with art recognized methods. With some embodiments, a polycarbonate having at least two hydroxyl groups is reacted with an aziridine, which results in the formation of an amine functional polycarbonate having at least two primary amine groups. With some further embodiments, the aliphatic polycarbonate having at least two reactive groups is prepared in a first step by ring-opening of trimethylene carbonate in the presence of a nitrophenyl functionalized initiator, followed by, in a second step, a reduction reaction resulting in the formation of primary amines, such as described in Macromolecules, 1997, 30, 6074. In accordance with some embodiments, at least one amine, such as a primary amine, of the aliphatic polycarbonate having at least two amine groups, can be blocked with an aldehyde group or a ketone group.

[064] The aliphatic polyurethane having at least two amine groups includes a plurality of urethane linkages (-O-C(O)-N(H)-). With some embodiments, the aliphatic polyurethane, having at least two amine groups, includes a linear or branched C_1-C_{20} alkyl linkage and/or a C_3-C_{10} cycloalkyl linkage, independently between and/or extending from each carbonate linkage. The aliphatic polyurethane having at least two amine groups can be prepared in accordance with art recognized methods. With some embodiments, a polyurethane having at least two hydroxyl groups is reacted with an aziridine, which results in the formation of an amine functional polyurethane having at least two primary amine groups. In accordance with some embodiments, at least one amine, such as a primary amine, of the aliphatic polyurethane having at least two amine groups, can be blocked with an aldehyde group or a ketone group.

[065] The polyethylenimine, can be referred to herein as a polyethylenimine having at least two amine groups. The polyethylenimine can be a linear or branched polyethylenimine. Suitable polyethyleneimines, with some embodiments, are formed by ring opening polymerization of ethyleneimine. Nonlimiting examples of suitable polyethyleneimines include those commercially available under the tradename EPOMIN™ (from Nippon Shokubai) and the like, which are selected, with some embodiments, so as to have amine equivalent weights and ranges and Mw values and ranges as described previously herein with regard to the polyamine component. In accordance with some embodiments, at least one amine, such as a primary amine, of the polyethylenimine having at least two amine groups, can be blocked with an aldehyde group or a ketone group.

[066] The curable photochromic compositions of the present invention include a polyisocyanate component that includes at least two isocyanate groups. With some embodiments, the polyisocyanate includes 2 to 10 isocyanate groups, or 2 to 8 isocyanate groups, or 2 to 6 isocyanate groups, or 2 to 5 isocyanate groups, or 2 to 4 isocyanate groups.

[067] With some embodiments, the polyisocyanate component includes at least one of: linear or branched aliphatic polyisocyanates; cycloaliphatic polyisocyanates; dimers thereof; trimers thereof; and combinations thereof. Dimers and trimers of polyisocyanates, such as diisocyanates, include, with some embodiments, linkages selected from isocyanurate, uretdione, biuret, allophanate, and combinations thereof. Dimers and trimers of polyisocyanates, such as diisocyanates, can be prepared in accordance with art-recognized methods, such as described in U.S. Patent No. 5,777,061 at column 3, line 44 through column 4, line 40. Examples of suitable linear or branched aliphatic polyisocyanates and cycloaliphatic polyisocyanates are provided a follows.

[068] Examples of linear or branched aliphatic polyisocyanates from which the polyisocyanate component of the curable photochromic composition can be selected include, but are not limited to: 1,2-diisocyanatoethane (ethylene diisocyanate); tetramethylene-1,4-diisocyanate; hexamethylene-1,6-diisocyanate; 2,2,4-trimethyl hexane-1,6-diisocyanate; 2,4,4-trimethyl hexane-1,6-diisocyanate; and dodecane-1,12-diisocyanate.

[069] Examples of cycloaliphatic polyisocyanates from which the polyisocyanate component of the curable photochromic composition can be selected include, but are not limited to: cyclobutane-1,3-diisocyanate; cyclohexane-1,3-diisocyanate; cyclohexane-1,4-diisocyanate; methyl cyclohexyl diisocyanate; hexahydrotoluene-2,4-diisocyanate; hexahydrotoluene-2,6-diisocyanate; hexahydrophenylene-1,3-diisocyanate; isophoronediisocyanate; hexahydrophenylene-1,4-diisocyanate; perhydrodiphenylmethane-2,4'-diisocyanate; perhydrodiphenylmethane-4,4'-diisocyanate; and norbornane diisocyanate.

[070] The polyisocyanate component of the curable photochromic composition has an isocyanate equivalent weight of less than or equal to 500 g/mole. With some embodiments, the polyisocyanate component has an isocyanate equivalent weight of from 80 g/mole to 500 g/mole, or from 80 g/mole to less than 500 g/mole, or from 80 g/mole to 400 g/mole, or from 80 g/mole to 350 g/mole.

[071] In accordance with the present invention, each isocyanate group of the polyisocyanate component is reversibly blocked (or capped) with a blocking agent (or capping agent).

[072] As used herein, the term “reversibly blocked” and related terms, such as “reversibly capped” with regard to the isocyanate groups of the polyisocyanate component, means isocyanate groups thereof that are blocked or capped with a blocking or capping agent. Under controlled conditions, such as exposure to elevated temperature, the blocking / capping agent separates (or deblocks or decaps) from the blocked isocyanate groups, allowing the free / unblocked isocyanate groups thereof to: react and form covalent bonds with reactive groups, such as the amine groups of the polyamine component. After unblocking or decapping from the blocked isocyanate groups of the polyisocyanate component, the blocking / capping agent can volatize out of the curable photochromic composition (prior to the composition becoming vitrified) and/or remain in the curable photochromic composition, such as a plasticizer. With some embodiments, it is desirable that the blocking / capping agent not form bubbles or voids in the curable photochromic composition and/or not overly plasticize the curable photochromic composition after deblocking / decapping.

[073] The blocking / capping groups of the blocked isocyanate groups of the polyisocyanate component can be selected from, with some embodiments, hydroxy (or hydroxyl) functional compounds, 1H-azoles, lactams, ketoximes, and mixtures thereof. Classes of hydroxy functional compounds include, but are not limited to, aliphatic, cycloaliphatic, or aromatic alkyl monoalcohols or phenolics. Specific examples of hydroxy functional compounds useful as blocking / capping agents, include, but are not limited to: lower aliphatic alcohols such as methanol, ethanol, and n-butanol; cycloaliphatic alcohols such as cyclohexanol and tetrahydrofuran; aromatic-alkyl alcohols, such as phenyl carbinol and methylphenyl carbinol; and glycol ethers, such as ethylene glycol butyl ether, diethylene glycol butyl ether, ethylene glycol methyl ether and propylene glycol methyl ether. With some embodiments, the hydroxy functional blocking / capping groups include phenolics, examples of which include, but are not limited to, phenol itself and substituted phenols, such as cresol, nitrophenol and p-hydroxy methylbenzoate.

[074] Examples of 1H-azoles that are useful as blocking / capping groups include, but are not limited to 1H-imidazole, 1H-pyrazole, 1H-dialkyl pyrazoles (such as, 1H-3,5-dimethyl pyrazole and 1H-2,5-dimethyl pyrazole), 1H-1,2,3-triazole, 1H-1,2,3-benzotriazole, 1H-1,2,4-triazole, 1H-5-methyl-1,2,4-triazole, and 1H-3-amino-1,2,4-triazole.

[075] Ketoximes useful as blocking / capping groups include those prepared from aliphatic or cycloaliphatic ketones. Examples of ketoxime capping groups include, but are limited to, 2-propanone oxime (acetone oxime), 2-butanone oxime (also referred to as, methylethyl ketoxime), 2-pentanone oxime, 3-pentanone oxime, 3-methyl-2-butanone oxime, 4-methyl-2-pentanone oxime, 3,3-dimethyl-2-butanone oxime, 2-heptanone oxime, 3-heptanone oxime, 4-heptanone oxime, 5-methyl-3-heptanone oxime, 2,6-dimethyl-4-heptanone oxime, cyclopentanone oxime, cyclohexanone oxime, 3-methylcyclohexanone oxime, 3,3,5-trimethylcyclohexanone oxime, and 3,5,5-trimethyl-2-cyclohexene-5-one oxime.

[076] Examples of lactam capping groups include, but are not limited to, e-caprolactam and 2-pyrolidinone. Other suitable capping groups include, morpholine, 3-aminopropyl morpholine, and N-hydroxy phthalimide.

[077] With some embodiments of the present invention, the blocked isocyanate groups of the polyisocyanate are each independently blocked with a blocking / capping agent selected from methylethyl ketoxime, e-caprolactam, pyrazole (more particularly, 1H-pyrazole), and dialkyl pyrazole (more particularly, 1H-dialkyl pyrazole, such as 1H-3,5-dimethyl pyrazole and 1H-2,5-dimethyl pyrazole).

[078] With some embodiments, the polyisocyanate component is present in the curable photochromic composition in an amount of from 40 percent by weight to 88 percent by weight, or from 45 percent by weight to 80 percent by weight, or from 55 percent by weight to 75 percent by weight, where the percent weights in each case are based on the total resin solids weight of the curable photochromic composition.

[079] The curable photochromic composition of the present invention, with some embodiments, has an equivalents ratio of: (i) equivalents of (meth)acrylate groups of the (meth)acrylate functional component; to (ii) equivalents of amine groups and of the polyamine component, that is from 1:3 to 1:15, or from 1:4 to 1:14, or from 1:5 to 1:12.

[080] The curable photochromic composition of the present invention, with some further embodiments, has an equivalents ratio of: (i) equivalents of amine groups of the polyamine component; to (ii) equivalents of isocyanate groups of the polyisocyanate component, that is from 1:0.7 to 1:3, or from 1:1 to 1:3, or from 1:2 to 1:2.9.

[081] The curable photochromic composition of the present invention, with some additional embodiments, has an equivalents ratio of: (i) equivalents of (meth)acrylate groups of the (meth)acrylate functional component; to (ii) equivalents of amine groups of the polyamine component; to (iii) equivalents of isocyanate groups of the polyisocyanate component that is from 1:3:2 to 1:15:45, or from 1:4:3 to 1:14:42, or from 1:5:4 to 1:12:36.

[082] The curable photochromic compositions of the present invention, with some embodiments, optionally include one or more catalysts (or cure catalysts) for catalyzing the reaction: between the blocked isocyanate groups of the polyisocyanate component and the amine groups of the polyamine component; and between amine groups of the polyamine component and (meth)acrylate groups of the (meth)acrylate functional component. Classes of useful catalysts include, but are not limited to: metal compounds, such as, but not limited to, organic tin compounds, organic bismuth compounds, organic zinc compounds, organic zirconium compounds, organic aluminum compounds, organic nickel compounds, and alkali metal compounds; and amine compounds, such as tertiary amine compounds, and quaternary ammonium compounds. Examples of organic tin compounds include, but are not limited to: tin(II) salts of carboxylic acids, such as, tin(II) acetate, tin(II) octanoate, tin(II) ethylhexanoate and tin(II) laurate; tin(IV) compounds, such as, dibutyltin oxide, dibutyltin dichloride, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate. Examples of suitable tertiary amine catalysts include, but are not limited to, diazabicyclo[2.2.2]octane and 1,5-diazabicyclo[4,3,0]non-5-ene. Examples of organic bismuth compounds include, but are not limited to, bismuth carboxylates. Examples of alkali metal compounds include, but are not limited to, alkali metal carboxylates, such as, but not limited to, potassium acetate, and potassium 2-ethylhexanoate. Examples of quaternary ammonium compounds include, but are not limited to, N-hydroxyalkyl quaternary ammonium carboxylates. With some embodiments, the catalyst is selected from tin(II) octanoate, dibutyltin(IV) dilaurate, and/or bismuth 2-ethylhexanoate.

[083] The catalyst can be present in the photochromic compositions of the present invention in any suitable amount, such as a catalytic amount. With some embodiments, the catalyst is in the photochromic compositions of the present invention in an amount of from 0.05 to about 5.0 percent by weight, or about 0.25 to about 3.0 percent by weight, the percent weights in each case being based on the total resin solids weight of the curable photochromic composition.

[084] The curable photochromic composition of the present invention can be cured by any suitable methods that result in the formation of covalent bonds between, (meth)acrylate groups of the (meth)acrylate functional component, amine groups of the polyamine component, and isocyanate groups of the polyisocyanate component. With some embodiments, the curable photochromic composition is cured by exposure to elevated temperature (in excess of ambient room temperature, such as above 25°C). Exposure to elevated temperatures, with some embodiments, results in deblocking of: blocked isocyanate groups of the polyisocyanate; and optionally blocked amine groups of the polyamine component. As used herein, by "cured" is meant a three dimensional crosslink network is formed by covalent bond formation, resulting from reaction between (meth)acrylate groups of the (meth)acrylate functional component, amine groups of the polyamine component, and isocyanate groups of the polyisocyanate component. When cured at elevated temperature, the curable photochromic composition can be referred to herein as a thermosetting curable photochromic composition. The temperature at which the thermosetting curable photochromic composition of the present invention is cured is variable and depends in part on the amount of time during which curing is conducted. With some embodiments, the curable photochromic composition is cured at an elevated temperature of from 80°C to 175 °C, or from 85°C to 150°C, or from 90°C to 130°C, for a period of 15 to 240 minutes.

[085] The curable photochromic compositions of the present invention include a photochromic compound(s). The photochromic compound can be selected from known classes and examples of photochromic compounds, and can include combinations or mixtures thereof.

[086] For example, although not limiting herein, mixtures of photochromic compounds can be used to attain certain activated colors, such as a near neutral gray or near neutral brown. See, for example, U.S. Patent No. 5,645,767, col. 12, line 66 to col. 13, line 19, which describes the parameters that define neutral gray and brown colors, which disclosure is specifically incorporated by reference herein.

[087] With some embodiments, the photochromic compound, of the curable photochromic compositions of the present invention, is selected from the group consisting of naphthopyrans, benzopyrans, phenanthropyrans, indenonaphthopyrans, spiro(indoline)naphthoxazines, spiro(indoline)pyridobenzoxazines, spiro(benzindoline)pyridobenzoxazines, spiro(benzindoline)naphthoxazines, spiro(indoline)-benzoxazines, fulgides, fulgimides, or diarylethenes, and mixtures of such photochromic compounds.

[088] The photochromic compound is present in the curable photochromic compositions of the present invention in an amount at least sufficient so as to provide an article prepared from the composition with a desirable level of photochromic properties, which in some embodiments is referred to as a photochromic amount. With some embodiments, the amount of photochromic compound(s) present in the curable photochromic composition is from 0.001 percent by weight to 40 percent by weight, or from 0.001 to 10 percent by weight, or from 0.01 to 8 percent by weight, or from 0.1 to 2.5 percent by weight, where the percent by weights are in each case based on the total resin solids weight.

[089] The curable photochromic compositions of the present invention can, with some embodiments, optionally include additives such as, but not limited to: waxes, such as for flow and wetting; flow control agents, such as poly(2-ethylhexyl)acrylate; antioxidants; adhesion promoters, such as (3-glycidoxypropyl) trimethoxysilane; surfactants; and ultraviolet (UV) light absorbers. Examples of useful antioxidants and UV light absorbers include, but are not limited to, those available commercially from BASF under the trademarks IRGANOX and TINUVIN. A non-limiting class of antioxidants are hindered amine light stabilizers (HALS), which can include one or more 2,2,6,6-tetralkylpiperindin-4-yl groups, such as one or more 2,2,6,6-tetramethylpiperidin-4-yl groups. These optional additives, when used, can be present in amounts up to 20 percent by weight, based on total resin solids weight.

[090] The curable photochromic compositions of the present invention can, with some embodiments, further include one or more fixed-tint dyes. As used herein, the term “fixed-tint dye” and related terms, such as “fixed-colorant,” “static colorant,” “fixed dye,” and “static dye” means dyes that are: non-photosensitive materials, which do not physically or chemically respond to electromagnetic radiation with regard to the visually observed color thereof. The term “fixed-tint dye” and related terms as used herein does not include and is distinguishable from photochromic compound. As used herein, the term “non-photosensitive materials” means materials that do not physically or chemically respond to electromagnetic radiation with regard to the visually observed color thereof, including, but not limited to, fixed-tint dyes.

[091] The optional fixed-tint dye of the curable photochromic composition, with some embodiments, includes at least one of azo dyes, anthraquinone dyes, xanthene dyes, azime dyes, iodine, iodide salts, polyazo dyes, stilbene dyes, pyrazolone dyes, triphenylmethane dyes, quinoline dyes, oxazine dyes, thiazine dyes, and polyene dyes.

[092] The curable photochromic compositions of the present can, with some embodiments, include one or more solvents, such as one or more organic solvents.

[093] Classes of organic solvents that can be present in the curable photochromic compositions of the present invention include, but are not limited to: ketones, such as, acetone, methyl ethyl ketone, and methyl isobutyl ketone; ethers, such as, dimethyl ether and methyl ethyl ether; cyclic ethers, such as, tetrahydrofuran, 3-oxotetrahydrofuran, and dioxane; esters, such as, ethyl acetate, ethyl lactate, ethylene carbonate and propylene carbonate; nitrogen containing cyclic compounds, such as, pyrrolidone, N-methyl-2-pyrrolidone, 1-butyl-pyrrolidin-2-one (commercially available as TAMISOLVE™ NxG dipolar aprotic solvent, from Eastman), and 1,3-dimethyl-2-imidazolidinone; sulfur containing compounds, such as, dimethyl sulfoxide and tetramethylene sulfone; aromatic compounds, such as, toluene, xylene, anisole, p-chlorotrifluoromethyl benzene, and butyl benzoate; and mixtures of aromatic compounds, such as, but not limited to, Aromatic 100 Fluid, which is a commercially available mixture of C_9-C_{10} dialkyl- and trialkyl-benzenes, and Aromatic 150 Fluid, which is a commercially available mixture of C_{10}-C_{12} alkylbenzenes and alkylnaphthalenes.

[094] Solvent(s) can be present in the curable photochromic compositions of the present invention, in an amount of from 5 to 95 percent by weight, or from 15 to 80 percent by weight, from 30 to 70 percent by weight, or from 30 to 60 percent by weight, in each case based on the total weight of the curable photochromic composition (including the weight of the solvent).

[095] The present invention also relates to articles, and in particular, photochromic articles that are prepared from the curable photochromic composition of the present invention as described previously herein. With some embodiments, the photochromic article is selected from layers (including films and/or sheets), and 3-dimensional articles.

[096] Classes of 3-dimensional articles, that can be prepared from the curable photochromic compositions of the present invention, include, but are not limited to, ophthalmic articles, display articles, windows, and mirrors.

[097] More typically, the curable photochromic compositions of the present invention are used to prepare photochromic layers, such as photochromic films and photochromic sheets. As used herein, the term “film” means a layer that is not self-supporting, such as, but not limited to, a coating. As used herein, the term “sheet” means a layer that is self-supporting, such as, but not limited to, an extruded sheet.

[098] The present invention also relates to an article, such as a photochromic article, that includes: (A) a substrate; and (B) a photochromic layer over at least one surface of the substrate, wherein the photochromic layer is formed from the curable photochromic composition of the present invention.

[099] The article, that includes a substrate, and a photochromic layer over at least one surface of the substrate (formed from the curable photochromic composition of the present invention) can, with some embodiments, be selected from ophthalmic articles, display articles, windows, and mirrors. Correspondingly, the substrate of the article can be selected from ophthalmic substrates, displays, windows, and mirrors. The substrate can be composed of one or more suitable materials, including, but not limited to: organic materials, such as organic polymeric materials, such as, but not limited to, thermoplastic polycarbonates, crosslinked polycarbonates, poly(meth)acrylates, and combinations thereof; glasses, such as silica-based glasses; metals; ceramic materials; and combinations thereof. Examples of substrates that can be included in the article (including optical elements) of the present invention include, but are not limited to, those described at column 35, line 5 through column 36, line 57 of US 8,628,685 B2, which disclosure is incorporated herein by reference.

[0100] The substrate, with some embodiments, can optionally include a photochromic material and/or a fixed-tint dye, which can each be selected from those classes and examples of photochromic materials and fixed-tint dyes as described previously herein. The optional photochromic material(s) / compound(s) present in the substrate can be the same or different than the photochromic compound(s) of the photochromic layer. The optional fixed-tint dye(s) can be the same or different than the optional fixed-tint dye(s) of the photochromic layer.

[0101] The photochromic layer of the article can, with some embodiments, be a photochromic coating, and the curable photochromic composition of the present invention is a curable photochromic coating composition.

[0102] The curable photochromic coating composition can be applied to the substrate in accordance with art-recognized methods, which include, but are not limited to, spray application methods, curtain coating application methods, draw-down blade (or bar) application methods, dip-coating application methods, spin-coating application methods, jet printing methods (such as inkjet printing methods, where the “ink” is replaced with a curable photochromic composition according to the present invention), and combinations thereof.

[0103] After application of the curable photochromic composition over at least one surface of the substrate, the applied curable photochromic composition is cured, such as described previously herein. The photochromic layer can be in the form of a single layer or multiple layers. When in the form of multiple layers, each layer of the photochromic layer can be prepared from curable photochromic compositions according to the present invention, having the same or different compositions, such as the same or different photochromic compound(s). The photochromic layer can have any suitable thickness, such as from 10 micrometers to 250 micrometers, or from 15 micrometers to 75 micrometers.

[0104] In addition to the photochromic layer, the article can optionally include one or more further art-recognized layers, such as, but not limited to: a primer layer(s); an adhesive layer(s); a protective layer(s) (such as a hard-coat layer); a polarizing layer(s); a birefringent layer(s); an antireflective layer(s); and/or another photochromic layer(s) that is prepared from a composition other than the curable photochromic composition of the present invention.

[0105] The present invention can be further characterized by one or more of the following non-limiting aspects.

[0106] Aspect 1: A curable photochromic composition comprising:

(a) a photochromic compound;

(b) an(meth)acrylate functional component comprising at least one (meth)acrylate group, and having an (meth)acrylate equivalent weight of 500 g/mole to 10,000 g/mole;

(c) a polyamine component comprising at least two amine groups, wherein each amine group is independently selected from primary amine and secondary amine, provided said polyamine component comprises at least two primary amine groups, and wherein said polyamine component has an amine equivalent weight of 30 g/mole to 250 g/mole;

(d) a polyisocyanate component comprising at least two isocyanate groups, and having an isocyanate equivalent weight of less than or equal to 500 g/mole, wherein each isocyanate group of said polyisocyanate component is reversibly blocked with a blocking agent; and

(e) optionally a catalyst.

[0107] Aspect 2: The curable photochromic composition of aspect 1, wherein an equivalents ratio of equivalents of (meth)acrylate groups of the (meth)acrylate functional component to equivalents of amine groups and of the polyamine component is from 1:3 to 1:15, or from 1:4 to 1:14, or from 1:5 to 1:12.

[0108] Aspect 3: The curable photochromic composition of aspect 1 or aspect 2, wherein an equivalents ratio of equivalents of amine groups of the polyamine component to equivalents of isocyanate groups of the polyisocyanate component is from 1:0.7 to 1:3, or from 1:1 to 1:3, or from 1:2 to 1:2.9.

[0109] Aspect 4: The curable photochromic composition of any one of aspects 1 to 3, wherein an equivalents ratio of: equivalents of (meth)acrylate groups of the (meth)acrylate functional component; to equivalents of amine groups of the polyamine component; to equivalents of isocyanate groups of the polyisocyanate component is from 1:3:2 to 1:15:45, or from 1:4:3 to 1:14:42, or from 1:5:4 to 1:12:36.

[0110] Aspect 5: The curable photochromic composition of any one of aspects 1 to 4, wherein the (meth)acrylate functional component comprises at least one of a polyether, a polyester, a polycarbonate, or a polyurethane, which in each case comprises at least one (meth)acrylate group.

[0111] Aspect 6: The curable photochromic composition of any one of aspects 1 to 5, wherein the (meth)acrylate functional component has an average molecular weight of 1000 g/mole to 10,000 g/mole, or from 1200 g/mole to 8000 g/mole, or from 1500 g/mole to 5000 g/mole.

[0112] Aspect 7: The curable photochromic composition of any one of aspects 1 to 6, wherein the (meth)acrylate functional component is present in an amount of from 10 percent by weight to 50 percent by weight, or from 15 percent by weight to 40 percent by weight, or from 20 percent by weight to 35 percent by weight, where the percent weights in each case are based on total resin solids weight of the curable photochromic composition.

[0113] Aspect 8: The curable photochromic composition of any one of aspects 1 to 7, wherein the(meth)acrylate functional component has 1 to 10 (meth)acrylate groups, or 1 to 8 (meth)acrylate groups, or 1 to 6 (meth)acrylate groups, or 1 to 5 (meth)acrylate groups, or 1 to 4 (meth)acrylate groups.

[0114] Aspect 9: The curable photochromic composition of any one of aspects 1 to 8, wherein the (meth)acrylate functional component comprises at least one of a polyether, a polyester, a polycarbonate, or a polyurethane, which in each case comprises at least one (meth)acrylate group.

[0115] Aspect 10: The curable photochromic composition of any one of aspects 1 to 9, wherein the (meth)acrylate functional component has an average molecular weight of 1000 g/mole to 10,000 g/mole.

[0116] Aspect 11: The curable photochromic composition of any one of aspects 1 to 10,wherein the (meth)acrylate functional component is present in an amount of from 10 percent by weight to 50 percent by weight, based on total resin solids weight of said curable photochromic composition.

[0117] Aspect 12: The curable photochromic composition of any one of aspects 1 to 7, wherein the(meth)acrylate functional component comprises, (i) a first (meth)acrylate functional component having one (meth)acrylate group, and optionally (ii) a second (meth)acrylate functional component having at least two (meth)acrylate groups.

[0118] Aspect 13: The curable photochromic composition of aspect 12, wherein: the first (meth)acrylate functional component having one (meth)acrylate group has an (meth)acrylate equivalent weight of 1000 g/mole to 10,000 g/mole, and an average molecular weight of 1000 g/mole to 10,000 g/mole; and the second (meth)acrylate functional component having at least two (meth)acrylate groups has an (meth)acrylate equivalent weight of 500 g/mole to 5000 g/mole, and an average molecular weight of 1000 g/mole to 10,000 g/mole.

[0119] Aspect 14: The curable photochromic composition of aspects 12 or 13, wherein the second(meth)acrylate functional component having at least two (meth)acrylate groups, has 2 to 10 (meth)acrylate groups, or 2 to 8 (meth)acrylate groups, or 2 to 6 (meth)acrylate groups, or 2 to 5 (meth)acrylate groups, or 2 to 4 (meth)acrylate groups.

[0120] Aspect 15: The curable photochromic composition of any one of aspects 1 to 14, wherein the polyamine component comprises at least one of aliphatic polyether, aliphatic polyester, aliphatic polycarbonate, aliphatic polyethylenimine, or aliphatic polyurethane, each independently having at least two amine groups.

[0121] Aspect 16: The curable photochromic composition of any one of aspects 1 to 15, wherein the polyamine component has a Mw of from 100 g/mole to 2500 g/mole, or from 100 g/mole to 2000 g/mole, or from 100 g/mole to 1500 g/mole.

[0122] Aspect 17: The curable photochromic composition of any one of aspects 1 to 16, wherein the polyamine component comprises at least one amine group that is blocked with an aldehyde group or a ketone group.

[0123] Aspect 18: The curable photochromic composition of any one of aspects 1 to 17, wherein the polyamine component is present in an amount of from 2 percent by weight to 12 percent by weight, or from 3 percent by weight to 11 percent by weight, or from 4 percent by weight to 10 percent by weight, where each percent weigh is in each case based on total resin solids weight of the curable photochromic composition.

[0124] Aspect 19: The curable photochromic composition of any one of aspects 1 to 18, wherein the polyamine component has an amine equivalent weight of 30 g/mole to 250 g/mole, or 40 g/mole to 200 g/mole, or 50 g/mole to 150 g/mol.

[0125] Aspect 20: The curable photochromic composition of any one of aspects 1 to 19, wherein the polyisocyanate component comprises at least one of, linear or branched aliphatic polyisocyanates, cycloaliphatic polyisocyanates, biurets thereof, allophanates thereof, isocyanurates thereof, and combinations thereof; and wherein each blocking agent of the polyisocyanate is independently selected from hydroxy functional compounds, 1H-azoles, lactams, and ketoximes.

[0126] Aspect 21: The curable photochromic composition of any one of aspects 1 to 20, wherein the catalyst comprises at least one of organotin catalysts, organobismuth catalysts, organozirconium catalysts, organozinc catalysts, or tertiary amine catalysts.

[0127] Aspect 22: The curable photochromic composition of aspect 21, wherein the catalyst comprises at least one of tin(II) octanoate, dibutyltin(IV) dilaurate, or bismuth 2-ethylhexanoate.

[0128] Aspect 23: The curable photochromic composition of any one of aspects 1 to 22, wherein the photochromic compound (a) comprises at least one of naphthopyrans, benzopyrans, phenanthropyrans, indenonaphthopyrans, spiro(indoline)naphthoxazines, spiro(indoline)pyridobenzoxazines, spiro(benzindoline)pyridobenzoxazines, spiro(benzindoline)naphthoxazines, spiro(indoline)-benzoxazines, fulgides, fulgimides, or diarylethenes.

[0129] Aspect 24: An article comprising:

(A) a substrate; and

(B) a photochromic layer over at least one surface of the substrate, wherein the photochromic layer is formed from the curable photochromic composition of any one of aspects 1 to 23.

[0130] The present invention is more particularly described in the following examples, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art. Unless otherwise specified, all parts and all percentages are by weight.

EXAMPLES

[0131] In Part 1 of the following examples there is described the synthesis of (meth)acrylate functional components. In Part 2 of the following examples there is described the preparation of curable photochromic compositions. In Part 3 of the following examples the preparation of test specimens coated with the curable photochromic compositions of Part 2 is described. In Part 4 of the following examples the evaluation and testing of the test specimens of Part 3 is described.

Part 1. Preparation of formulation components

Example 1

Preparation of a hydroxyl polycaprolactone mono-acrylate

[0132] 4-Hydroxybutyl acrylate (13.25 g), 2,6-di-*t*-butyl-4-methylphenol (BHT) (0.0925 g), and ε-caprolactone (179.5 g) were dissolved in dichloromethane (DCM, 125 mL) while under nitrogen before diphenyl phosphate (DPP, 4.59 g) was added in one portion. After stirring at room temperature for 8 hours, the solution was washed with saturated $NaHCO_3$ (2 x 100 mL) followed by brine (100 mL). After drying the combined organic extracts over $MgSO_4$, they were filtered through a short silica plug, eluent was DCM and then ramped to 20% ethyl acetate (EtOAc). The solvent was removed, and the resulting white material (198 g) was dissolved in EtOAc (300 mL, at 45°C) and the clear solution was poured into cold hexanes (2 L, 0°C). The precipitated white powder was filtered, washed with hexanes (1 L, 0°C), and dried under vacuum to yield 181.4 g (95%). The chemical structure, molecular weight (2011 g/mole), and acrylate equivalent weight (2011 g/mole) were verified by ^1H NMR.

Example 2

Preparation of a polycaprolactone mono-acrylate

[0133] 4-Hydroxybutyl acrylate (13.25 g), BHT (0.092 g), and ε-caprolactone (168.9 g) were dissolved in DCM (125 mL) while under nitrogen before DPP (4.60 g) was added in one portion. After stirring at room temperature for 8 hours, *N,N*-dimethylaminopyridine (DMAP, 2.25 g) was added followed by hexanoic acid (13.37 g) and N,N'-dicyclohexylcarbodiimide (DCC) (23.86 g). The crude material was stirred at room temperature overnight. The formed *N,N'*-dicyclohexylurea (DCU) was filtered out and the filtrate was washed with HCl (1M, 100 mL), saturated $NaHCO_3$ (100 mL) followed by brine (100 mL). After drying the combined organic extracts over $MgSO_4$, they were filtered through a short silica plug (eluent was DCM ramped to 20% EtOAc). The solvent removed, and the resulting white material (207 g) was dissolved in EtOAc (250 mL) and the clear solution was poured into cold methanol (2 L, 0°C). The precipitated white powder was filtered, washed with methanol (1 L, 0°C), and dried under vacuum to yield 178 g (94%). The chemical structure, molecular weight (2050 g/mole), and acrylate equivalent weight (2050 g/mole) were verified by ^1H NMR.

Example 3

Preparation of a polycarbonate diacrylate

[0134] A polycarbonate diol with a reported molecular weight of 2000 g/mole and an average hydroxyl equivalent weight of 1000 g/mole, available from UBE Industries, Ltd. as ETERNACOLL® PH200D (PH-200D, 40 g), acrylic acid (3.5 g), DCC (10.3g), 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS, 2.4 g), and DCM (200 mL) were combined and stirred overnight under nitrogen. The precipitated DCU was removed by filtration, and the resultant solution was filtered through a short silica plug (eluent was DCM ramped to 50% EtOAc). The solvent was removed, the resulting viscous liquid was dissolved in EtOAc (40 mL), and then filtered through a short pad of celite to remove any leftover DCU. The concentrated clear solution (40 g) was poured into cold methanol (50 mL, 0°C). After allowing the layers to separate, the methanol layer was decanted off and the product dried under vacuum to yield 35 g (83%), a colorless viscous liquid. An acrylate equivalent weight of 1054 g/mole was calculated by ^1H NMR.

Part 2. Preparation of Curable Compositions

Comparative Examples 1-7

[0135] Coating compositions of Comparative Examples (CE) 1-7 were prepared using the components listed in Table 1, shown in parts by weight. For each, the components of Charge 1 were combined and heated to 80°C until the solids dissolved completely, for a minimum of 2 hours. The solution was cooled to room temperature and the charge 2 components were added at room temperature, followed by stirring for 1 hour at 70°C. The charge 3 components were added at room temperature and the mixtures were stirred for an additional 1 hour prior to use.

Table 1

Charge	Componenet	CE-1	CE-2	CE-3	CE-4	CE-5	CE-6	CE -7
1	Photochromic dyes[i]	4.00	4.00	4.00	4.00	4.00	4.00	4.00
	TINUVIN® 144[ii]	2.00	2.00	2.00	2.00	2.00	2.00	2.00
	IRGANOX® 245[iii]	2.00	2.00	2.00	2.00	2.00	2.00	2.00
	N-methyl pyrrolidinone	34.11	34.11	34.11	34.11	34.11	34.11	34.11
2	Acrylate of Example 1	--	--	--	--	30.3	--	15.1
	Acrylate of Example 2	--	--	--	--	--	30	--
	Butyl acrylate	--	1.86	0.93	0.93	--	--	--
	EPOMIN™ SP-006[iv]	10	--	--	--	--	--	--
	JEFFAMINE ED-600[v]	--	36.84	36.84	--	36.84	--	36.84
	JEFFAMINE T-3000[vi]	--	--	--	--	--	148.5	--
	Diethylenetriamine[vii]	--	--	--	4.78	--	--	--
3	1,6-Hexanediol-diacrylate[viii]	--	--	0.82	0.82	--	--	0.82
	(3-Glycidoxypropyl) trimethoxysilane	4.52	4.52	4.52	4.52	4.52	4.52	4.52
	BYK® 333[ix]	0.07	0.07	0.07	0.07	0.07	0.07	0.07
	TRIXENE® BI-7960[x]	85.7	85.7	85.7	85.7	85.7	85.7	85.7
	Dibutyltin dilaurate	0.3	0.3	0.3	0.3	0.3	0.3	0.3
% NV solids (theoretical)		65.4	65.4	65.4	65.4	65.4	65.4	65.4
Mole ratio 1 (acrylate:amine)		--	1:9.6	1:9.6	1:9.6	1:9.6	1:9.6	1:9.6
Mole ratio 2 (amine:isocyanate)		1:1.5	1:1.5	1:1.5	1:1.5	1:1.5	1:1.5	1:1.5

[i] A blend of photochromic indenofused naphthopyran dyes formulated to give a grey color on activation

[ii] A hindered amine light stabilizer, commercially available from BASF

[iii] An antioxidant commercially available from BASF

[iv] A polyethylenimine with a molecular weight of 600 g/mole and amine (primary and secondary) equivalent weight of 71.5 g/mole, available from Nippon Shokubai Co LTD.

[v] A polyether diamine with a molecular weight of 600 g/mole and amine equivalent weight of 264 g/mole, available from Huntsman Corporation.

[vi] A polyether triamine with a molecular weight of 3000 g/mole and amine equivalent weight of 1064 g/mole, available from Huntsman Corporation.

[vii] Amine equivalent weight (both primary & secondary) of 34.4 g/mole

[viii] Acrylate equivalent weight of 113.1g/mole

[ix] A polyether modified dimethylpolysiloxane copolymer, available from BYK-Chemie.

[x] A blocked hexamethylene diisocyanate biuret with an isocyanate equivalent weight (on solids) of 287 g/mole, provided at 70% solids in propylene glycol monomethyl ether from Baxenden Chemical Co.

Examples 8-13

[0136] Photochromic compositions employing different ratios of acrylate component were prepared using the components listed in Table 2 using the procedures of Comparative Examples 1-7 above.

Table 2

Charge	Component	**Ex.8**	**Ex. 9**	**Ex. 10**	**Ex.11**	**Ex. 12**	**Ex. 13**
1	Photochromic dyes	4.00	4.00	4.00	4.00	4.00	4.00
	TINUVIN® 144	2.00	2.00	2.00	2.00	2.00	2.00
	IRGANOX® 245	2.00	2.00	2.00	2.00	2.00	2.00
	N-methyl pyrrolidinone	34.0	34.0	34.0	34.0	34.1	34.0
2	Acrylate Example 1	--	--	30	-	-	-
	Acrylate Example 2	30	25	--	35	30	25
	EPOMIN™ SP-006	6	6	6	10	10	10
3	(3-Glycidoxypropyl) trimethoxysilane	4.5	4.5	4.5	4.5	4.52	4.5
	BYK® 333	0.07	0.07	0.07	0.07	0.07	0.07
	TRIXENE® BI-7960	91.5	98.6	91.5	78.5	85.7	92.9
	Dibutyltin dilaurate	0.3	0.3	0.3	0.3	0.3	0.3
% NV solids (theoretical)		64.7	63	63.5	66.2	65.4	64.6
Mole ratio 1 (acrylate:amine)		1:5.8	1:7	1:5.8	1:8.3	1:9.6	1:11.7
Mole ratio 2 (amine:isocyanate)		1:2.6	1:2.9	1:2.6	1:1.4	1:1.5	1:1.6

Examples 14-16

[0137] Photochromic compositions employing different ratios of mono-acrylate and di-acrylate components were prepared using the components listed in Table 3 using the procedures of Comparative Examples 1-7 above.

Table 3

		Ex.14	Ex. 15	Ex. 16
1	Photochromic dyes	4.00	4.00	4.00
	TINUVIN® 144	2.00	2.00	2.00
	IRGANOX® 245	2.00	2.00	2.00
	N-methyl pyrrolidinone	34.0	34.0	34.0
2	Acrylate Example 2	17.5	15.0	12.5
	Acrylate Example 3	17.5	15.0	12.5
	EPOMIN™ SP-006	10	10	10
3	(3-Glycidoxypropyl) trimethoxysilane	4.5	4.5	4.5
	BYK® 333	0.07	0.07	0.07
	TRIXENE® BI-7960	78.5	85.7	92.9
	Dibutyltin dilaurate	0.3	0.3	0.3
% NV solids (theoretical)		66.2	65.4	64.6
Mole ratio 1 (acrylate:amine)		1:6.25	1:7.26	1:8.75
Mole ratio 2 (amine:isocyanate)		1:1.37	1:1.5	1:1.6

Examples 17-18

[0138] Photochromic compositions using some low molecular weight and low equivalent weight amines were prepared using the components listed in Table 4 using the procedures of Comparative Examples 1-7 above.

Table 4

Charge	Component	**Ex.17**	**Ex. 18**
1	Photochromic dyes	4.00	4.00
	TINUVIN® 144	2.01	2.01
	IRGANOX® 245	2.01	2.01
	N-methyl pyrrolidinone	34.1	34.1
2	Acrylate Example 2	30	30
	Hexamethylenediamine	8.1	--
	Diethylenetriamine	--	4.78
3	(3-Glycidoxypropyl) trimethoxysilane	4.52	4.52
	BYK® 333	0.07	0.07
	TRIXENE® BI-7960	85.7	85.7
	Dibutyltin dilaurate	0.3	0.3
% NV solids (theoretical)		65.4	65.4
Mole ratio 1 (acrylate:amine)		1:9.6	1:9.6
Mole ratio 2 (amine:isocyanate)		1:1.5	1:1.5

Part 3. Preparation of photochromic test specimens

[0139] The compositions of Comparative Examples 1-7 and Examples 8-18, were applied to PDQ® coated Gentex® polycarbonate plano lenses, each having a diameter of 76 millimeters. Prior to coating, each lens was treated with corona using Tantec equipment with 70 KV and 1000 W settings. About 1-2 mL of each composition was dispensed onto the substrate and then rotated at a spin speed sufficient to deposit 0.45-0.55g of wet coating (weight depends on %NV solids) onto the lens for all the Comparative Examples 1-7 and Examples 8-18.

[0140] The test specimens of Comparative Examples 1-7 and Examples 8-18 were prepared in duplicate, then cured at 85°C for 30 minutes and 125°C for 30 minutes in a forced air oven.

Part 4. Properties of Test Specimens

Part 4a. Micro hardness evaluation

[0141] One set of test specimens were subjected to an additional thermal cure for three hours at 105°C and set aside for hardness measurements. These specimens were then subjected to micro-hardness testing using a Fischerscope HCV, Model H100SMC available from Fischer Technology, Inc. The hardness was measured at a penetration depth of 2 microns after a 100 mNewton load for 15 seconds. Each test specimen was measured at least twice and the resulting data was averaged.

Part 4b. Photochromic performance

[0142] The second set of test specimens (Comparative Examples 1-7 and Examples 8-18) were further treated with corona as previously described and spin coated with a protective coating, Hi-Gard 1080S from PPG Industries, Inc., and then each test specimen was thermally cured at 105 °C for three hours.

[0143] The photochromic performance of the test specimens was tested on the Bench for Measuring Photochromics (BMP) made by Essilor, Ltd. France. The BMP was maintained at a constant temperature of 73.4 °F (23°C) during testing. Prior to testing, each of the coated test specimens were exposed to 365 nanometer ultraviolet light for about 10 minutes at a distance of about 14 centimeters to activate the photochromic materials. The UVA (315 to 380 nm) irradiance at the lens was measured with a LICOR® Model Li-1800 spectroradiometer and found to be 22.2 watts per square meter. Each test specimen was then placed under a 500 watt, high intensity halogen lamp for about 10 minutes at a distance of about 36 centimeters to bleach (inactivate) the photochromic materials. The illuminance at the specimen was measured with the LICOR® spectroradiometer and found to be 21.9 Klux. Each test specimen was then kept in a dark environment at room temperature (from 70 to 75 °F, or 21 to 24 °C) for at least one hour prior to testing on the BMP. Prior to measurement, each lens was measured for ultraviolet absorbance at 390 nanometers (Abs 390 nm).

[0144] The BMP optical bench was fitted with two 150 watt Newport Model #6255 Xenon arc lamps set at right angles to each other. The light path from Lamp 1 was directed through a 3 mm SCHOTT® KG-2 band-pass filter and appropriate neutral density filters that contributed to the required UV and partial visible light irradiance level. The light path from Lamp 2 was directed through a 3 mm SCHOTT® KG-2 band-pass filter, a SCHOTT® short band 400 nm cutoff filter and appropriate neutral density filters in order to provide supplemental visible light illuminance. A 2 inch x 2 inch 50% polka dot beam splitter set at 45° to each lamp is used to mix the two beams. The combination of neutral density filters and voltage control of the Xenon arc lamp were used to adjust the intensity of the irradiance. Software (i.e., BMP Soft version 2.1e) was used on the BMP to control timing, irradiance, air cell and sample temperature, shuttering, filter selection, and response measurement. A ZEISS® spectrophotometer, Model MCS 601, with fiber optic cables for light delivery through the lens was used for response and color measurement. Photopic response measurements were collected on each lens.

[0145] The power output of the optical bench, i.e., the dosage of light that the lens was exposed to, was adjusted to 6.7 watts per square meter (W/m^2) UVA, integrated from 315-380 nm, and 50 Klux illuminance, integrated from 380-780 nm. Measurement of this power set point was made using an irradiance probe and the calibrated Zeiss spectrophotometer. The lens sample cell was fitted with a quartz window and self-centering sample holder. The temperature in the sample cell was controlled at 23 °C through the software with a modified Facis, Model FX-10, environment simulator. Measurement of the sample’s dynamic photochromic response and color measurements were made using the same Zeiss spectrophotometer with fiber optic cables for light delivery from a tungsten halogen lamp through the sample. The collimated monitoring light beam from the fiber optic cable was maintained perpendicular to the test sample while passing through the sample and directed into a receiving fiber optic cable assembly attached to the spectrophotometer. The exact point of placement of the sample in the sample cell was where the activating xenon arc beam and the monitoring light beam intersected to form two concentric circles of light. The angle of incidence of the xenon arc beam at the sample placement point was about 30° from perpendicular.

[0146] Response measurements, in terms of a change in optical density (ΔOD) from the unactivated or bleached state to the activated or colored state were determined by establishing the initial unactivated transmittance, opening the shutter from the Xenon lamp(s) and measuring the transmittance through activation at selected intervals of time. Change in optical density was determined according to the formula:

$$\Delta OD = \log_{10}(\%Tb / \%Ta)$$

where $\%T_b$ is the percent transmittance in the bleached state and $\%T_a$ is the percent transmittance in the activated state. Optical density measurements were based on photopic optical density.

[0147] The results of the micro-hardness for Comparative Examples 1-7 and Examples 8 through 18 are shown in Tables 5 through 8. The ΔOD at saturation was after 15 minutes of activation and the Fade Half Life (T1/2) value is the time interval in seconds for the ΔOD of the activated form of the photochromic material in the coating to reach one half the fifteen-minute ΔOD at 73.4°F (23°C), after removal of the activating light source.

Comparative Examples 1-7

[0148] The comparative example results shown in Table 5 collectively demonstrate that if any component is absent or outside the claimed equivalent weight, the resulting coating either demonstrates such hardness as photochromic activity is suppressed, or the resulting coating is very soft.

Table 5

Comp. Example	Fischer micro-hardness (N/mm^2)	ΔOD	T1/2 @ Photopic (seconds)
CE-1	>150	No activation	
CE-2	1	0.85	37
CE-3	0.3	0.9	39
CE-4	150	No activation	
CE-5	0.7	0.73	29
CE-6	1.1	0.73	38
CE-7	1.4	0.64	25

[0149] The formulations of Examples 8-13 demonstrate the effect of varied acrylate to amine mole ratio. As can be seen by the results in Table 6 below, all tested acrylate:amine ratios at varying levels of amine and/or acrylate content produced coatings with good hardness and photochromic performance.

Table 6

Example	Fischer micro-hardness (N/mm^2)	ΔOD	T1/2 @ Photopic (seconds)
8	49	0.88	35
9	60	0.88	37
10	39	0.82	40
11	39	0.83	33
12	50	0.90	36
13	62	0.89	39

Examples 14-16

[0150] Examples 14-16 included a mixture of mono- and di-acrylates. The results in Table 7 indicate that the addition of a di-acrylate of suitable equivalent weight gives good hardness and photochromic performance.

Table 7

Example	Fischer micro-hardness (N/mm^2)	ΔOD	T1/2 @ Photopic (seconds)
14	53	0.87	35
15	62	0.85	37
16	74	0.85	40

Examples 17-18

[0151] The formulations of Examples 17 and 18 demonstrate the effect of low molecular weight, low equivalent weight and lower functionality amines when compared to previous examples employing polyethyleneimine at a similar mole ratio, as summarized in Table 8.

Table 8

Example	Fischer micro-hardness (N/mm^2)	ΔOD	T1/2 @ Photopic (seconds)	Acrylate:amine Mole ratio	Amine:NCO Mole ratio
17	40	0.84	31	1:9.6	1:1.5
18	38	0.85	32	1:9.6	1:1.5

[0152] The results in Tables 5 through 8 clearly demonstrate the benefit of relatively high equivalent weight of acrylate and relatively low amine equivalent weight, in combination with blocked isocyanate in order to achieve both acceptable photochromic performance and hardness.

[0153] The present invention has been described with reference to specific details of particular embodiments thereof. It is not intended that such details be regarded as limitations upon the scope of the invention except insofar as to the extent that they are included in the accompanying claims.

WHAT IS CLAIMED IS:

1. A curable photochromic composition comprising:

(a) a photochromic compound;

(b) a (meth)acrylate functional component comprising at least one (meth)acrylate group, and having a (meth)acrylate equivalent weight of 500 g/mole to 10,000 g/mole;

(c) a polyamine component comprising at least two amine groups, wherein each amine group is independently selected from primary amine and secondary amine, provided said polyamine component comprises at least two primary amine groups, and wherein said polyamine component has an amine equivalent weight of 30 g/mole to 250 g/mole;

(d) a polyisocyanate component comprising at least two isocyanate groups, and having an isocyanate equivalent weight of less than or equal to 500 g/mole, wherein each isocyanate group of said polyisocyanate component is reversibly blocked with a blocking agent; and

(e) optionally a catalyst.

2. The curable photochromic composition of claim 1, wherein an equivalents ratio of equivalents of (meth)acrylate groups of the (meth)acrylate functional component to equivalents of amine groups and of said polyamine component is from 1:3 to 1:15.

3. The curable photochromic composition of claim 1, wherein an equivalents ratio of equivalents of amine groups of said polyamine component to equivalents of isocyanate groups of said polyisocyanate component is from 1:0.7 to 1:3.

4. The curable photochromic composition of claim 1, wherein an equivalents ratio of: equivalents of (meth)acrylate groups of said (meth)acrylate functional component; to equivalents of amine groups of said polyamine component; to

equivalents of isocyanate groups of said polyisocyanate component is from 1:3:2 to 1:15:45.

5. The curable photochromic composition of claim 1, wherein said (meth)acrylate functional component comprises at least one of a polyether, a polyester, a polycarbonate, or a polyurethane, which in each case comprises at least one (meth)acrylate group.

6. The curable photochromic composition of claim 5, wherein said (meth)acrylate functional component has an average molecular weight of 1000 g/mole to 10,000 g/mole.

7. The curable photochromic composition of claim 1, wherein said (meth)acrylate functional component is present in an amount of from 10 percent by weight to 50 percent by weight, based on total resin solids weight of said curable photochromic composition.

8. The curable photochromic composition of claim 1, wherein said polyamine component comprises at least one of aliphatic polyether, aliphatic polyester, aliphatic polycarbonate, aliphatic polyethylenimine, or aliphatic polyurethane, each independently having at least two amine groups.

9. The curable photochromic composition of claim 1, wherein said polyamine component has a Mw of from 100 g/mole to 2500 g/mole.

10. The curable photochromic composition of claim 1, wherein said polyamine component comprises at least one amine group that is blocked with an aldehyde group or a ketone group.

11. The curable photochromic composition of claim 1, wherein said polyamine component is present in an amount of from 2 percent by weight to 12 percent by weight, based on total resin solids weight of said curable photochromic composition.

12. The curable photochromic composition of claim 1, wherein said polyisocyanate component comprises at least one of, linear or branched aliphatic polyisocyanates, cycloaliphatic polyisocyanates, biurets thereof, allophanates thereof, isocyanurates thereof, and combinations thereof; and wherein each blocking agent of said polyisocyanate is independently selected from hydroxy functional compounds, 1H-azoles, lactams, and ketoximes.

13. The curable photochromic composition of claim 1, wherein said catalyst comprises at least one of organotin catalysts, organobismuth catalysts, organozirconium catalysts, organozinc catalysts, or tertiary amine catalysts.

14. The curable photochromic composition of claim 1, wherein said photochromic compound (a) comprises at least one of naphthopyrans, benzopyrans, phenanthropyrans, indenonaphthopyrans, spiro(indoline)naphthoxazines, spiro(indoline)pyridobenzoxazines, spiro(benzindoline)pyridobenzoxazines, spiro(benzindoline)naphthoxazines, spiro(indoline)-benzoxazines, fulgides, fulgimides, or diarylethenes.

15. An article comprising:

(A) a substrate; and

(B) a photochromic layer over at least one surface of the substrate, wherein the photochromic layer is formed from the curable photochromic composition of claim 1.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2023/065727

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F290/06 C08G18/00 C08G18/24 C08G18/32 C08G18/50
C08G18/64 C08G18/80 C08K5/1545 C09D175/02 G02B1/10

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)

C08K C08F C08G C09D G02B

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2022/042841 A1 (TRANSITIONS OPTICAL LTD [IE]) 3 March 2022 (2022-03-03) paragraphs [0001], [0003] - [0006], [0035] - [0049], [0063] - [0074], [0085] examples 1-13,17-24; tables 1-5 -----	1-15
A	EP 1 922 349 A1 (TRANSITIONS OPTICAL INC [US]) 21 May 2008 (2008-05-21) paragraphs [0001] - [0006], [0031] - [0035], [0047] - [0079], [0093] examples 1,3,4; tables 1-3 -----	1-15
A	US 2007/045596 A1 (KING ERIC M [US] ET AL) 1 March 2007 (2007-03-01) paragraphs [0002] - [0008] examples 1-5; tables I,II -----	1-15

☐ 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 30 November 2023	Date of mailing of the international search report 13/12/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Neugebauer, Ute

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/065727

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