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(71) Applicant *(for all designated States except US)*: **EMPIRE TECHNOLOGY DEVELOPMENT LLC** [US/US]; 2711 Centerville Road, Suite 400, Wilmington, Delaware 19808 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **CARLSON, William Brenden** [US/US]; 11753 25th Avenue NE, Seattle, Washington 98125 (US). **SJONG, Angele** [US/US]; 601 Dahlia Way, Louisville, Colorado 80027 (US). **WAN, Feng** [US/US]; 4209 257th Place SE, Issaquah, Washington 98029 (US). **LONDERGAN, Timothy** [US/US]; 5014 48th Avenue NE, Seattle, Washington 98105 (US).

(74) Agent: **HELMSEN, Joseph T.**; Pepper Hamilton LLP, Suite 5000, 500 Grant Street, Pittsburgh, Pennsylvania 15219-0717 (US).

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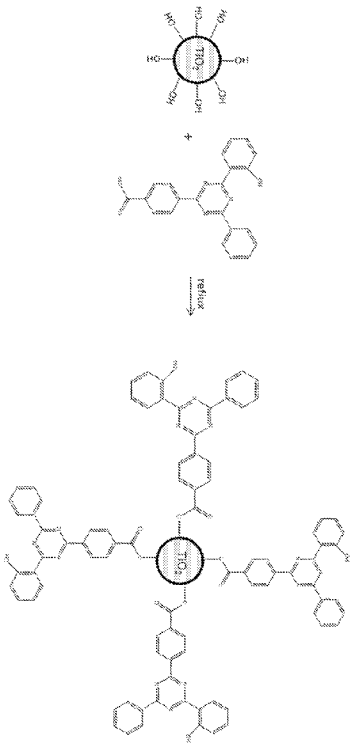
[Continued on next page]

(54) Title: UV ABSORBERS ON PIGMENTS

FIGURE 2



(57) Abstract: Coating compositions with light absorbing chromophores and method of making the compositions are disclosed. The compositions include a photocatalytic pigment attached to at least one light absorber covalently or non-covalently. The light absorber provides protection to the coating polymer from UV-induced photocatalytic activity of the pigments.

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UV ABSORBERS ON PIGMENTS

BACKGROUND

[0001] Decorative coatings and paints are used by consumers and industrial users to beautify and protect substrates. The most simple coatings and paints are made of a polymer (the binder) in a solvent (the vehicle), which is commonly called a lacquer. Paints and coatings are used to modify the appearance of an object by adding color, gloss, or texture and by blending with or differentiating from a surrounding environment. For example, a surface that is highly light scattering (i.e. a flat surface) can be made glossy by the application of a paint that has a high gloss. Conversely, a glossy surface can be made to appear flat. Thus, the painted surface is hidden, altered, and ultimately changed in some manner by the presence of the coating. In addition, decorative paints protect the surface from the surrounding elements and reduce corrosion.

[0002] Many paints and coatings include pigments with photocatalytic properties, such as titanium dioxide, in their composition. The photocatalytic properties of titanium dioxide result from the promotion of electrons from the valence band to the conduction band under the influence of ultraviolet (UV) and near-UV radiation. The reactive electron-hole pairs that are created migrate to the surface of the titanium dioxide particles where the holes oxidize adsorbed water to produce reactive hydroxyl radicals and the electrons reduce adsorbed oxygen to produce superoxide radicals, both of which can degrade nitrogen compounds and volatile organic compounds in the air. In view of these properties, photocatalytic titanium dioxide has been employed in coatings to remove pollutants from the air. However, the hydroxyl radicals produced can also react with the organic binder, resulting in degradation of the coating. This problem is exacerbated when the coating to exposed to intense UV radiation from direct sunlight. Therefore, there exists a need for

improved coating compositions with photocatalytic pigments that are resistant to UV-induced degradation.

SUMMARY

[0003] The present disclosure is directed towards paints and coating compositions with photocatalytic pigments that display improved durability when exposed to UV radiation. In one embodiment, a pigment material may be at least one photocatalytic pigment covalently or non-covalently attached to at least one light absorber.

[0004] In another embodiment, a method of preparing a photocatalytic pigment material in contact with the light absorber may involve contacting at least one photocatalytic pigment with at least one light absorber to form a mixture, and heating the mixture to form a pigment material.

[0005] In an additional embodiment, a coating composition may include at least one photocatalytic pigment covalently or non-covalently attached to at least one light absorber, and at least one binder component.

[0006] In a further embodiment, a method of coating a substrate may involve applying a coating composition to the substrate, wherein the coating composition comprises at least one photocatalytic pigment covalently or non-covalently attached to at least one light absorber.

BRIEF DESCRIPTION OF THE FIGURES

[0007] FIG. 1 depicts the tautomerization of 2-(4,6-diphenyl-[1,3,5]triazin-2-yl)-phenol when exposed to UV light. The tautomer dissipates energy harmlessly through internal conversion.

[0008] FIG. 2 illustrates covalent binding of 2-(4,6-diphenyl-[1,3,5]triazin-2-yl)-phenol to titanium dioxide according to an embodiment.

[0009] FIG. 3 illustrates a light absorbing triazin dissolved in tetraethylorthosilicate and coated onto a titanium dioxide particle according to an embodiment.

[0010] FIG. 4 illustrates a coating with light absorbing chromophore according to an embodiment.

DETAILED DESCRIPTION

[0011] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

[0012] Pigmentary titanium dioxide is the most widely used white pigment in commerce today due to its extraordinary combination of properties including little or no adsorption of visible light, high refractive index, high opacity, and the ability to confer durability to coatings containing this pigment. However, due to the photocatalytic property of titanium dioxide, the organic binders decompose in the presence of UV radiation to carbon dioxide, water and nitrogen containing species, thus degrading the coating. One way to mitigate this problem is to use silicone-based binders, since they provide greater stability in the presence of active species produced from catalytic reactions. However, the use of silicone-based binders is not favored due to increased costs when compared to organic polymers. Therefore, there exists a need for improved photocatalytic pigments that can be safely used with organic binders when exposed to UV radiation.

[0013] The present disclosure is directed towards paints and coating compositions with photocatalytic pigments that display improved durability when exposed to UV radiation. In some embodiments, a pigment material may be at least one photocatalytic pigment covalently or non-covalently attached to at least one light absorber.

[0014] In some embodiments, the photocatalytic pigment may be titanium dioxide, copper oxide, hematite, magnetite, wüstite, chromium oxide, tin dioxide, carbonate pigments, or any combination thereof. Titanium dioxide is produced in two crystal phases, rutile and anatase, that differ in lattice structures, refractive indices, and densities. The titanium dioxide used in the coatings may be a rutile titanium dioxide particle, an anatase titanium dioxide particle, or a mixture thereof. The titanium dioxide particles may have an average particle diameter of about 300 nanometers to about 1 micron, of about 300 nanometers to about 750 nanometers, or of about 300 nanometers to about 500 nanometers. Specific examples include about 300 nanometers, about 400 nanometers, about 500 nanometers, about 600 nanometers, about 750 nanometers, about 800 nanometers, about 1 micron, and ranges between (and including the endpoints of) any two of these values. In some embodiments, a composition comprising a plurality of photocatalytic pigment particles, such as titanium dioxide, will have at least 50%, at least 60%, at least 70%, at least 80%, at least 90%, at least 95%, at least 96%, at least 97%, at least 98%, at least 99%, or at least 99.5% of the particles with the recited particle diameter or within the range of particle diameters.

[0015] The photocatalytic pigment may be attached covalently or non-covalently to a light absorber (also called a light absorbing chromophore). The light absorber may be able to absorb electromagnetic radiation such as UV, IR or visible light. Examples of light absorber that may be used include, but not limited to, hydroxybenzophenones, hydroxybenzotriazoles, triazins or a combination thereof. A typical function of a triazin as a light absorber is explained in FIG. 1. When 2-(4,6-diphenyl-[1,3,5]triazin-2-yl)-phenol absorbs a quanta of light, a molecular rearrangement takes place to form a tautomer, 6-(4,6-diphenyl-1H-[1,3,5]triazin-2-ylidene)-cyclohexa-2,4-dienone. 6-(4,6-Diphenyl-1H-[1,3,5]triazin-2-ylidene)-cyclohexa-2,4-dienone relaxes back to 2-(4,6-diphenyl-

[1,3,5]triazin-2-yl)-phenol, and the energy is given off as "heat" or vibrational energy. As a result, no reaction products are produced by the tautomerization because the whole event is internal to the molecule. The hydroxyl radicals or other reactive species are not generated, and thus the life of the coating may be greatly extended by the use of such light-absorbing chromophores.

[0016] Examples of hydroxybenzophenones include, but are not limited to, 2-hydroxy- benzophenone; 4-hydroxybenzophenone; 4-methoxy-2-hydroxybenzophenone; 4-octyloxy-2-hydroxybenzophenone; 4-decyloxy-2-hydroxybenzophenone; 4-dodecyloxy-2-hydroxybenzo- phenone; 4-benzyloxy-2-hydroxybenzophenone; 4,2',4'-trihydroxy-2-hydroxybenzophenone; 2'-hydroxy-4,4'-2-hydroxybenzophenone; dimethoxy-2-hydroxybenzophenone; and 4-methoxy-2-hydroxybenzophenone.

[0017] Non-limiting examples of hydroxybenzotriazoles include 2-(2'-hydroxy-5'-methylphenyl)benzotriazole; 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl) benzotriazole; 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole; 2'-hydroxypheny1)-5-chlorobenzotriazole; 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole; 2- (3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole; 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole; and 2-(3',5'-ditert-

amyl-2'-hydroxyphenyl)benzotriazole.

[0018] Some of the triazin compounds that may be used as a light absorber are 2,4,6-tris{N[4-(2-ethylhex-1 - yl)oxycarbonylphenyl]amino}-1,3,5-triazine; bis(2'-ethylhexyl) 4,4'-((6-(((tert-buty1)aminocarbonyl)pheny-1amino)-l,3,5-triazine-2,4-diy1)imino)benzoate; 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-l,3,5-triazine; 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-l,3,5-triazine; 2-(2,4-dihydroxypheny1)-4,6-bis(2,4-dimethylpheny1)-l,3,5-triazine; 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-l,3,5-triazine; 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-

1,3,5-triazine; 2-(4,6-diphenyl-[1,3,5] triazin-2-yl)-phenol; and 2-(2-hydroxy-4-dodecyloxypheny1)-4,6-bis(2,4-dimethylpheny1)-1,3,5-triazine.

[0019] In some embodiments, the light absorber may be attached to the surface of the photocatalytic pigment covalently. The photocatalytic pigments, such as metal oxides, usually contain hydroxyl groups on their surface. The light absorber may be attached by reacting the carboxyl group of the light absorber with a hydroxyl group to form an ester. A Dean-Stark apparatus or any other equivalent reflux apparatus may be used for this process. In some embodiments, the light absorber described herein is dissolved in a solvent that forms an azeotrope with water. Examples of such solvents include toluene, xylene, chloroform, and methylene chloride. Further, a small amount of catalyst such as *p*-toluene sulfonic acid may be included to facilitate the reaction. The reflux reaction may be performed from about 1 hour to about 10 hours, from about 1 hour to about 8 hours, from about 1 hour to about 6 hours, or from about 1 hour to about 5 hours. Specific examples include about 1 hour, about 1.5 hours, about 5 hours, about 6 hours, about 7.5 hours, about 8 hours, about 10 hours, and ranges between (and including the endpoints) any two of these values. The light absorber and the photocatalytic pigment may be mixed in a weight to weight ratio of about 1:1000 to about 3:10, of about 1:1000 to about 1:10, or of about 1:1000 to about 1:100. Specific examples include about 1:1000, about 1:100, about 1:20, about 1:10, about 3:10, and ranges between any two of these values. After the reflux reaction, the mixture may be cooled to room temperature and the product may be filtered and dried. FIG. 2 illustrates the surface treatment of titanium dioxide particles with a triazin compound.

[0020] In other embodiments, the pigment material may contain a linker moiety between the photocatalytic pigment and the light absorber. The linker moiety may be a silane, an ester, an oxide, an ether, a germane, a stannane, a thio compound, a sulfate, a sulfonate, a

sulfonyl compound, a seleno compound, a selenate, a selenonate, a selenonyl compound or a combination thereof.

[0021] In some embodiments, the light absorbing chromophore may be non-covalently associated with the surface of the photocatalytic pigment. For example, the light absorber is dissolved in a hydrated oxide solution, and the solution is coated on the surface of the photocatalytic pigment. The hydrated oxide may be hydrated silicon dioxide, hydrated aluminum oxide, hydrated calcium oxide, hydrated zinc oxide, or hydrated magnesium oxide, or any mixture thereof. The light absorber may also be incorporated in a sol-gel layer that surrounds the photocatalytic pigment. The sol-gel layer or coating may be prepared from any transition metal alkoxide. FIG. 3 illustrates one such embodiment. For example, the titanium dioxide particles are coated with tetraethylorthosilicate, and the light absorber is incorporated in this coating. The hydrated oxide coating further helps to keep the hydroxyl and superoxide radicals formed by the photocatalytic activity of titanium dioxide inside the pigment particle and prevent their release. This reduces or prevents the damage to the organic binders and extends the life of the paint.

[0022] The pigment material described herein may be dispersed in one or more organic binders, preferably a polymeric organic binder. In the broadest aspect, it is contemplated that any polymeric binder may be employed. In some embodiments, the polymeric binder is a water-dispersible polymer. The water-dispersible polymer may include a latex binder, such as natural latex, neoprene latex, nitrile latex, acrylic latex, vinyl acrylic latex, styrene acrylic latex, styrene butadiene latex, or the like. Compositions may include a single binder or a mixture of two or more polymeric binders that may be of the same class or different. For example, organic binders may be combined with a silicon-based binder.

[0023] In some embodiments, the pigment material may be dispersed in inorganic binders. Inorganic binders may include, without limitation, alkali metal silicates, such as potassium silicate, sodium silicate, lithium silicate or the like.

[0024] Paints and coatings of the present disclosure may contain one or more additives that alter the properties of the paint, such as shelf life, application and longevity, and health and safety. Such additives may be added, for example, during the manufacture of the emulsion polymer or during the formulation of the paint itself. Additives include initiators, rheology modifiers, preservatives, coalescing agents, stabilizers and the like. Initiators, such as persulfates, may be added to the coatings of the present disclosure. Initiators are a source of free radicals to initiate the polymerization process in which monomers condense to form the polymers. Coatings may also contain a redox system initiator, such as ferrous and thiosulfate along with the persulfate salts, that promote polymerization at room temperature.

[0025] In some embodiments, one or more thickeners and rheology modifiers may be added to achieve the desired viscosity and flow properties. Thickeners function by forming multiple hydrogen bonds with the acrylic polymers, thereby causing chain entanglement, looping and/or swelling which results in volume restriction. Thickeners, such as cellulose derivatives including hydroxyethyl cellulose, methyl cellulose and carboxymethyl cellulose, may be used in the compositions.

[0026] In some embodiments, one or more preservatives may be added in the coating compositions in low doses to protect against the growth of microorganisms. Preservatives, such as methyl benzisothiazolinones, chloromethylisothiazolinones, barium metaborate and 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride, may be used.

[0027] In some embodiments, one or more stabilizers, such as ethylene and propylene glycol, may be used. Stabilizers help to reduce or prevent formation of ice crystals

at low temperatures in water-borne paints, thereby retaining the dispersion stability and reducing damage to the polymers.

[0028] In some embodiments, one or more coalescing agents, such as ester alcohols, benzoate ethers, glycol ethers, glycol ether esters and n-methyl-2-pyrrolidone, may be added to the coating compositions. Coalescing agents are added to, for example, insure film formation under varying atmospheric conditions. They may be slow evaporating solvents with some solubility in the polymer phase. They may act as a temporary plasticizer, allowing film formation at temperatures below the system's glass transition temperature, after which they slowly diffuse to the surface and evaporate, increasing the hardness and block resistance of the film.

[0029] In some embodiments, coatings of the present disclosure may further contain one or more of the following: solvents, pigments, plasticizers, surfactants and the like. Surfactants may be used, for example, to create the micelles for particle formation, as well as long-term particle stabilization and these provide stability through electrostatic and steric hindrance mechanisms. In some embodiments, ionic and non-ionic surfactants may be used. Examples include, but are not limited to, alkyl phenol ethoxylates, sodium lauryl sulfate, dodecylbenzene sulfonate, polyoxyethylene alkyl ethers, polyoxyethylene alkyl allyl ethers, acetylene glycols, polyoxyethylene and polyoxypropylene.

[0030] In some embodiments, one or more plasticizers may be added to the compositions to adjust the tensile properties of the paint film. Plasticizers may be, for example, glucose-based, glycerine-based, propylene glycol, ethylene glycol, phthalates and the like.

[0031] The coating compositions of the disclosure may also comprise one or more extenders or fillers which serve to thicken coating films and support the structure of the coating composition. Some extenders may also provide hiding power and function as

pigments, particularly above the critical pigment volume concentration, and most extenders are color neutral. Common extenders include clays, such as kaolin clays, china clays, tales, quartz, barytes (barium sulphate) and carbonate salts such as calcium carbonate, zinc carbonate, magnesium carbonate or mixtures thereof.

[0032] A coating of the present disclosure may generally be applied to any substrate. The substrate may be an article, an object, a vehicle or a structure. Although no particular limitation is imposed on the substrate to be used in the present disclosure, glasses, plastics, metals, ceramics, wood, stones, cement, fabric, paper, leather, and combinations or laminations thereof may be used. The coating may be applied to a substrate by spraying, dipping, rolling, brushing, or any combination thereof.

[0033] FIG. 4 illustrates a paint embodiment. The paint is applied to the substrate and cures into a solid film. The light absorbing chromophore-titanium dioxide pigments are exposed at the surface and imbedded throughout the coating. A new layer of light absorbing chromophore-titanium dioxide pigments are created as the surface wears. Thus, the surface remains protected from harmful light. Being an organic coating, it has excellent adhesion to the substrate and prevents water, electrolytes, organics, and other contaminates from harming the substrate.

EXAMPLES

EXAMPLE 1: Preparation of pigment material – sample 1

[0034] About 100 grams of commercially available titanium dioxide (average particle diameter of about 500 nanometers) is mixed with 10 grams of 4-[4-(2-hydroxy-phenyl)-6-phenyl-[1,3,5]triazin-2-yl]-benzoic acid in 150 ml of toluene. The mixture is refluxed using a Dean-Stark apparatus in the presence of trace amount of *p*-toluene sulfonic acid for about 5 hours. At the end of this period, the mixture is cooled to room temperature and the product is filtered, washed with toluene and dried in a vacuum oven for 2 hours.

EXAMPLE 2: Preparation of pigment material – sample 2

[0035] About 100 grams of commercially available titanium dioxide (average particle diameter of about 500 nanometers) is mixed with 10 grams of 4'-(2-hydroxy-benzoyl)-biphenyl-4-carboxylic acid in 150 ml of toluene. The mixture is refluxed using a Dean-Stark apparatus in the presence of trace amount of *p*-toluene sulfonic acid for about 5 hours. At the end of this period, the mixture is cooled to room temperature and the product is filtered, washed with toluene and dried in a vacuum oven for 2 hours.

EXAMPLE 3: Preparation of a coating

[0036] A coating is prepared having the following components: 40 grams of titanium dioxide pigment attached to a light absorber (from Example 1), 0.75 grams of thickener (hydroxyethyl cellulose), 0.5 grams of pigment dispersant aid (Surfynol CT-136),150 grams of solvent (water), 117 grams of acrylic emulsion (Rhoplex TP-257), 3 grams of coalescing agent (1:1 blend of butyl carbitol and Texanol) and 0.05 grams of bactericide.

[0037] The coating is prepared as follows. About 0.75 grams of hydroxyethyl cellulose is slowly added to 150 mL of water under shear. Once the hydroxyethyl cellulose is dissolved, about 0.5 grams of Surfynol CT-136 is added, followed by the addition of 40 grams of titanium dioxide pigment attached to a light absorber. The pigment is added slowly in 0.5 gram batches.

Separately, under gentle shear and dropwise addition, about 3.0 grams of a 1:1 blend of butyl carbitol and Texanol is added to 117 grams of the acrylic emulsion, and is followed by addition of 0.05 grams of bactericide. To this acrylic blend, the previously prepared pigment dispersion is slowly added in 0.5 gram increments using a peristaltic pump.

EXAMPLE 4: Measuring the photocatalytic activity of the pigment material in a coating

[0038] The photocatalytic activity of the pigment in a paint sample (from Example 3) is investigated based on its ability to degrade the organic dye methylene blue. As the organic dye is degraded to water, carbon dioxide, and nitrogen containing species due to the photocatalytic activity of the pigment, a loss of color is observed. The photocatalytic activity is monitored by measuring the brightness of the dye color.

[0039] The protocol is as follows: a film of paint is coated on a substrate such as a glass plate. The film thickness is similar to that used in the final application and generally not less than 25 microns thick when dry and the paint film is allowed to dry at least overnight. A solution of methylene blue in water (0.373 grams/L) is prepared and applied on the coated substrate and allowed to sit for about 60 minutes. The excess of methylene blue solution is removed and the substrate surface is dried and brightness value of the surface is measured. The substrate surface is exposed to UV light for about 48 hours at an intensity of 30 to 60 W/m^2 (300-400 nm wavelengths), and the brightness value is re-measured. The brightness value will remain unchanged, thus demonstrating the protection of the coating from UV-induced degradation.

EXAMPLE 5: Evaluating a coating after exposure to UV light

[0040] A coating with a pigment material (from Example 2) is applied on a glass plate, and the plate is exposed to UV light for about 24 hours at an intensity of 30 to 60 W/m^2 (300-400 nanometer wavelengths) in an Atlas Suntest cabinet. A similar coating with untreated titanium dioxide pigment particles is also applied on a glass plate and exposed to UV light. Coating degradation is monitored by measuring the carbonyl content using Fourier Transform Infra-red Spectroscopy and spectral reflectance using at BYK 4545 Gloss Meter. The coating with untreated titanium dioxide pigments will degrade and chalk more when compared to coating with pigment material from Example 2.

EXAMPLE 6: AN OBJECT COATED WITH A PAINT

[0041] A boat is coated with a paint containing treated titanium dioxide pigment particles (from Example 3). A similar coating containing untreated titanium dioxide pigments is applied on an another boat. The boats are exposed to UV light (300-400 nanometer wavelength) for several days. The boat coated with paint having untreated titanium dioxide pigments will chalk and fade faster when compared to the boat coated with paint containing treated titanium dioxide particles.

[0042] In the above detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be used, and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

[0043] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope

of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0044] As used in this document, the singular forms "a," "an," and "the" include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term "comprising" means "including, but not limited to."

[0045] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0046] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0047] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (*e.g.*, bodies of the appended claims) are generally intended as "open" terms (*e.g.*, the term "including" should be interpreted as "including but not limited to," the term "having" should be interpreted as "having at least," the term "includes" should be interpreted as "includes but is not limited to," etc.). It will be

further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or "an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (*e.g.*, "a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (*e.g.*, the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (*e.g.*, " a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (*e.g.*, " a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase

presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0048] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also thereby described in terms of any individual member or subgroup of members of the Markush group.

[0049] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as "up to," "at least," and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0050] Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

CLAIMS

What is claimed is:

1. A pigment material comprising at least one photocatalytic pigment attached to at least one light absorber covalently or non-covalently.

2. The material of claim 1, wherein the light absorber is a hydroxybenzophenone, a hydroxybenzotriazole, a triazin or a combination thereof.

3. The material of claim 1, wherein the photocatalytic pigment is titanium dioxide, copper oxide, hematite, magnetite, wüstite, chromium oxide, tin dioxide, carbonate pigments, or a combination thereof.

4. The material of claim 1, wherein the photocatalytic pigment is a rutile titanium dioxide particle, an anatase titanium dioxide particle, or a mixture thereof.

5. The material of claim 1, wherein the photocatalytic pigment comprises titanium dioxide having an average particle diameter of about 300 nanometers to about 1 micron.

6. The material of claim 1, wherein the photocatalytic pigment comprises particles of titanium dioxide coated with a layer of at least one hydrated silicon dioxide, hydrated aluminum oxide, hydrated calcium oxide, hydrated zinc oxide, hydrated magnesium oxide, or any mixture thereof.

7. The material of claim 6, wherein the light absorber is present within the hydrated oxide layer.

8. The material of claim 1, wherein the photocatalytic pigment comprises particles of titanium dioxide coated with a layer of sol-gel made from a transition metal alkoxide.

9. The material of claim 8, wherein the light absorber is present within the sol-gel layer.

10. The material of claim 9, wherein the sol-gel layer is a layer of tetraethylorthosilicate.

11. The material of claim 1, wherein the photocatalytic pigment is a titanium dioxide particle with a triazin moiety attached to it.

12. The material of claim 1, wherein the photocatalytic pigment is a titanium dioxide particle with a hydroxybenzophenone molecule attached to it.

13. The material of claim 1, further comprising a linker between the photocatalytic pigment and the light absorber.

14. The material of claim 13, wherein the linker is a silane, an ester, an oxide, an ether, a germane, a stannane, a thio compound, a sulfate, a sulfonate, a sulfonyl compound, a seleno compound, a selenate, a selenonate, a selenonyl compound or a combination thereof.

15. The material of claim 1, wherein the material is incorporated into a paint or a coating substance.

16. The material of claim 1, wherein the material is incorporated into a decorative paint, wherein the material provides protection to the decorative paint from UV-light.

17. A method of preparing a photocatalytic pigment material in contact with the light absorber, the method comprising:

contacting at least one photocatalytic pigment with at least one light absorber to form a mixture; and

heating the mixture to form a pigment material.

18. The method of claim 17, wherein the photocatalytic pigment is titanium dioxide, copper oxide, hematite, magnetite, wüstite, chromium oxide, tin dioxide, carbonate pigment, or any combination thereof.

19. The method of claim 17, wherein the photocatalytic pigment is a rutile titanium dioxide particle, an anatase titanium dioxide particle, or a mixture thereof.

20. The method of claim 17, wherein the light absorber is a hydroxybenzophenone, a hydroxybenzotriazole, a triazine or a combination thereof.

21. The method of claim 17, wherein contacting the at least one photocatalytic pigment with the at least one light absorber comprises combining the photocatalytic pigment with the light absorber in the presence of a solvent and a catalyst.

22. The method of claim 21, wherein the catalyst is *p*-toluene sulfonic acid.

23. The method of claim 21, wherein the solvent is toluene, xylene, chloroform or methylene chloride.

24. The method of claim 17, wherein contacting the photocatalytic pigment with the light absorber comprises combining the light absorber with the photocatalytic pigment in a weight to weight ratio of about 1:1000 to about 3:10.

25. The method of claim 17, wherein heating the mixture comprises heating the mixture under a reflux for about 1 hour to about 10 hours to form a formed product.

26. The method of claim 25, further comprising cooling the formed product to room temperature.

27. The method of claim 25, further comprising filtering the formed product.

28. A coating composition comprising:

at least one photocatalytic pigment attached to at least one light absorber covalently or non-covalently; and

at least one binder component.

29. The composition of claim 28, wherein the light absorber is a hydroxybenzophenone, a hydroxybenzotriazole, a triazine or a combination thereof.

30. The composition of claim 28, wherein the photocatalytic pigment is titanium dioxide, copper oxide, hematite, magnetite, wüstite, chromium oxide, tin dioxide, carbonate pigments, or a combination thereof.

31. The composition of claim 28, wherein the photocatalytic pigment is a rutile titanium dioxide particle, an anatase titanium dioxide particle, or a mixture thereof.

32. The composition of claim 28, further comprising a linker between the photocatalytic pigment and the light absorber.

33. The composition of claim 28, wherein the binder comprises one or more silicone polymers, one or more organic polymers, or a combination thereof.

34. The composition of claim 28, further comprising a solvent, a coalescing agent, a fungicide, a rheology modifier, a plasticizer, or a surfactant, or any combination thereof.

35. The composition of claim 28, wherein the coating is a decorative coating, an industrial coating, a protective coating, a self-cleaning coating, or any combination thereof.

36. A method of coating a substrate, the method comprising:

applying a coating composition to the substrate, wherein the coating composition comprises at least one photocatalytic pigment attached to at least one light absorber covalently or non-covalently.

37. The method of claim 36, wherein the light absorber is a hydroxybenzophenone, a hydroxybenzotriazole, a triazine or a combination thereof.

38. The method of claim 36, wherein the photocatalytic pigment is titanium dioxide, copper oxide, hematite, magnetite, wüstite, chromium oxide, tin dioxide, carbonate pigments, or a combination thereof.

39. The method of claim 36, wherein the photocatalytic pigment is a rutile titanium dioxide particle, an anatase titanium dioxide particle, or a mixture thereof.

40. The method of claim 36, wherein the composition further comprises a linker between the photocatalytic pigment and the light absorber.

41. The method of claim 36, wherein the coating composition further comprises a binder, a solvent, a coalescing agent, a fungicide, a rheology modifier, a plasticizer, a surfactant, or any combination thereof.

42. The method of claim 36, wherein the coating composition is applied to the substrate by coating, brushing, dipping, spraying, rolling, or any combination thereof.

43. The method of claim 36, wherein the coating is a decorative coating, an industrial coating, a protective coating, a self-cleaning coating, or any combination thereof.

FIGURE 1

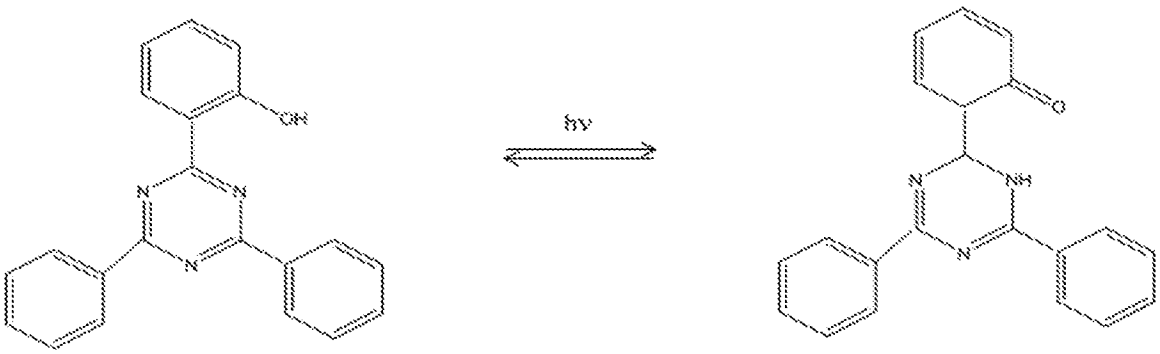


FIGURE 2

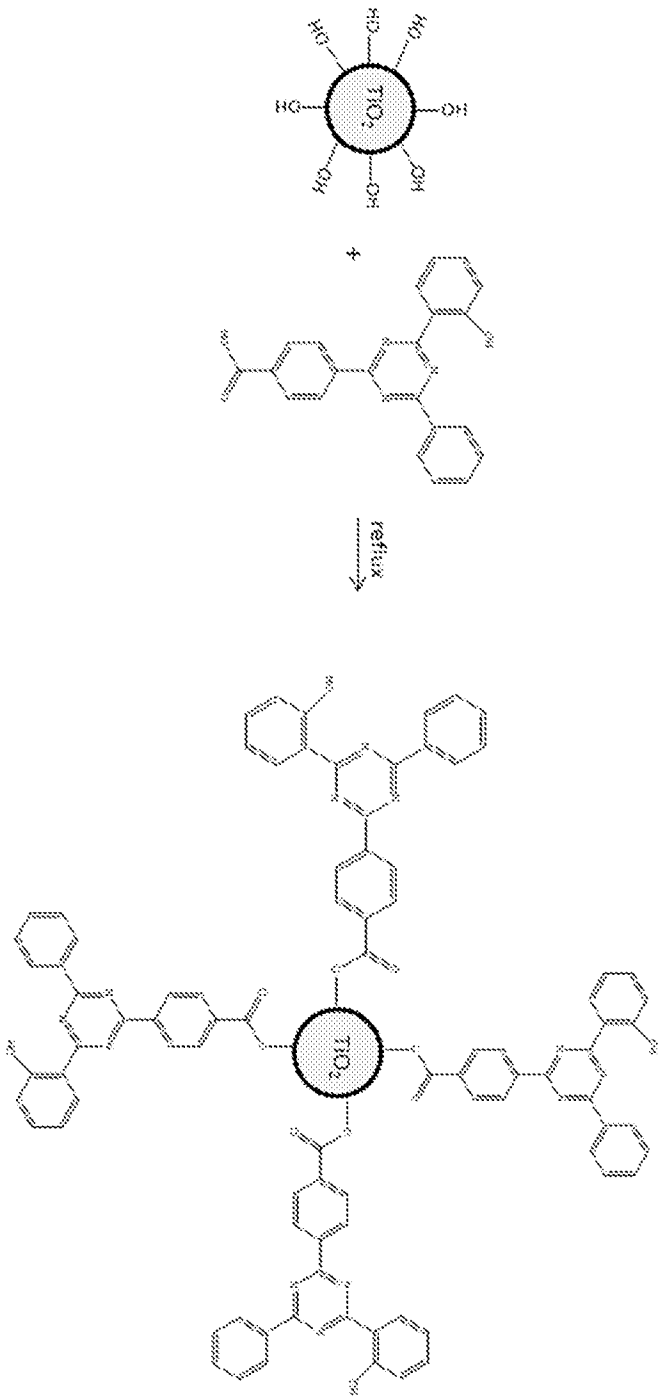


FIGURE 3

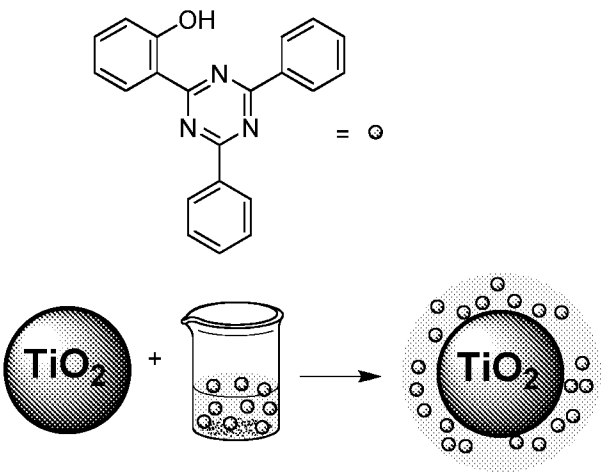
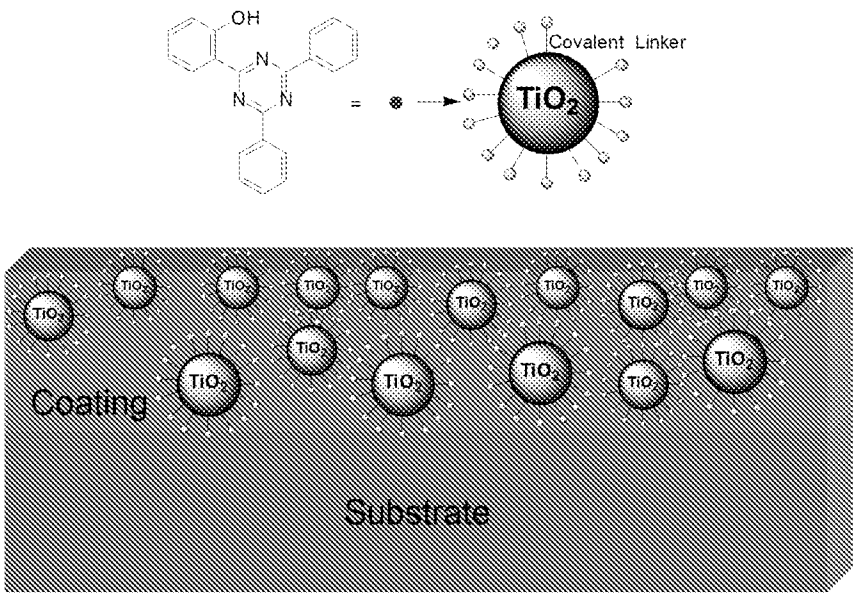


FIGURE 4



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/50780

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C09D 7/12, 5/00 (2012.01)
USPC - 106/31.01, 31.6
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)
IPC(8) - C09D 7/12, 5/00
USPC - 106/31.01, 31.6

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC(8) - C09D 7/12, 5/00, USPC - 106/31.01, 31.6: keyword search, as below

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, USPTO PubWest, Google Scholar -- Search Terms used: titanium, oxide, dioxide, triazine, triazin, hydroxybenz$, photocatalytic, catalytic, absorb, adsorp, link, linked, functionalized, attached, associated, pigmet, particle, nanoparticle, microparticle, powder, rutile, anatase, gel, sol, tetraethylorthosilicate, silicate, calcium, zinc, m

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2010/0135939 A1 (LEHMANN et al.) 03 June 2010 (03.06.2010), para [0001]; [0002]; [0003]; [0006]; [0101]; [0105]; [0105]; [0106]; [0008]; [0104]; [0110];	1-3, 5, 8, 9, 11-15 --- 4, 6, 7, 10, 16
Y	US 2011/0245391 A1 (KARPOV et al.) 06 October 2011 (06.10.2011), para [0018]; [0019]; [0023]; [0052; [0036]; [0088]; [0052]; [0053]	6, 7, 10
Y	US 2005/0249943 A1 (NISHIKAWA et al.) 10 November 2005 (10.11.2005), para [0015]; [0017]; [0096]	4
Y	US 2010/0184887 A1 (GONZALEZ et al.) 22 July 2010 (22.07.2010), abstract; para [0078]; [0033]; [0051]; [0053]; [0064]	16
Y	US 200/90291107 A1 (SCHEHLMANN et al.) 26 November 2009 (26.11.2009), para [0007], [0008]-[0013], [0043], [0060]-[0066], [0122], [0123]	1-16
Y	US 2009/0286068 A1 (NIGUMA et al.) 19 November 2009 (19.11.2009), para [0001], [0095]-[0100]	1-16
A	US 2012/0118318 A1 (HILLEBRANDT et al.) 17 May 2012 (17.05.2012), entire document	1-16
A	US 2010/0087310 A1 (KISCH et al.) 08 April 2010 (08.04.2010), entire document	1-16
A	US 2008/0124575 A1 (HOLLMAN et al.) 29 May 2008 (29.05.2008), entire document	1-16

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 March 2013 (04.03.2013)	25 MAR 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/50780

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

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

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

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

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

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

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-16, directed to a pigment material comprising at least one photocatalytic pigment attached to at least one light absorber covalently or non-covalently.

Group II: claims 17-27, directed to a method of preparing a photocatalytic pigment material in contact with a light absorber, the method comprising: contacting at least one photocatalytic pigment with at least one light absorber to form a mixture; and heating the mixture to form a pigment material.

- Please see extra sheet for continuation -

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

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

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

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-16

Remark on Protest

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

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

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/50780

Continuation of Box III: Lack of Unity of Invention

Group III: claims 28-35, directed to a coating composition comprising: at least one photocatalytic pigment attached to at least one light absorber covalently or non-covalently; and at least one binder component.

Group IV: claims 36-43, directed to a method of coating a substrate, the method comprising: applying a coating composition to the substrate, wherein the coating composition comprises at least one photocatalytic pigment attached to at least one light absorber covalently or non-covalently.

The inventions listed as Groups I - IV do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The special technical features of the claims of Groups I-IV are indicated in the Group descriptions, above.

The only common technical element shared by all the above groups is that they are related to at least one photocatalytic pigment attached to at least one light absorber covalently or non-covalently. Groups III and IV share the common technical element of being related to a coating composition. These common technical elements do not represent an improvement over the prior art of US 2010/0184887 A1 to Gonzalez et al., which teaches nanoparticles comprising attached light-absorbing compounds (abstract), wherein the particles may comprise photocatalytic (para [0078]) metal and semimetal oxides, including titanium oxides (para [0033]), the organic molecules may be bonded to the inorganic oxides by a linking group (para [0051]). The organic molecules may comprise UV or light absorbers (para [0063], [0064]). Although Gonzalez does not explicitly refer to the oxide nanoparticles as pigments, Gonzalez does indicate wherein at least some other prior art does (para [0004]). Further, Gonzalez teaches the use of the particles in the formulation of coating compositions (para [0127]). It would have been obvious to a person of ordinary skill in the art to consider the nanoparticles taught by Gonzalez as being pigment nanoparticles, based on the specific composition thereof.

Therefore, the inventions of Groups I-IV lack unity of invention under PCT Rule 13 because they do not share a same or corresponding special technical feature.