



(51) International Patent Classification:

A01N 43/04 (2006.01)

(21) International Application Number:

PCT/US2012/060046

(22) International Filing Date:

12 October 2012 (12.10.2012)

(25) Filing Language:

English

(26) Publication Language:

English

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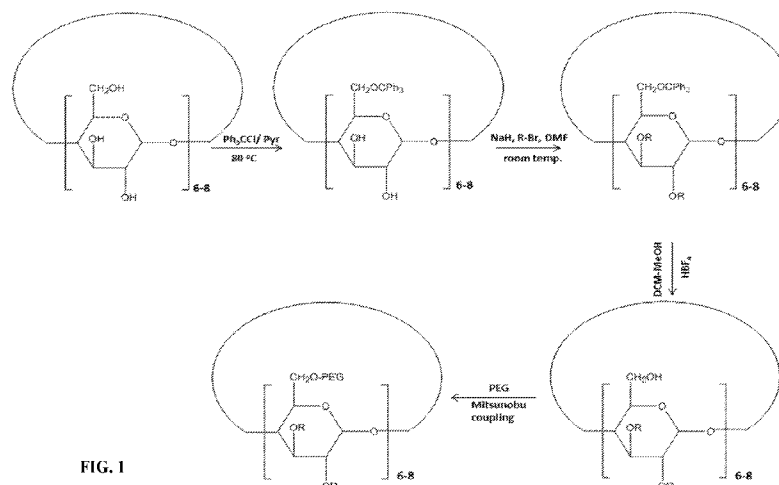
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(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PAINTS AND COATINGS CONTAINING CYCLODEXTRIN ADDITIVES



(57) Abstract: Hydrophilic coating compositions and methods to make and use the compositions are disclosed. The coatings include one or more amphiphilic cyclodextrins, with one or more hydrophilic groups in place of primary hydroxyl groups, and one or more hydrophobic groups in place of secondary hydroxyl groups. The hydrophobic surface of the cyclodextrin faces the binder particles, while the hydrophilic surface is exposed to the exterior, thus providing a hydrophilic and self-cleaning property to the coating.

PAINTS AND COATINGS CONTAINING CYCLODEXTRIN ADDITIVES

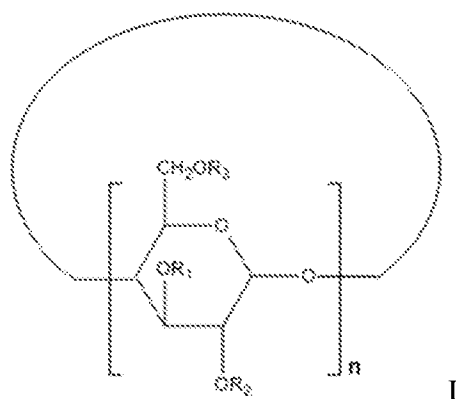
BACKGROUND

[0001] Coatings and paints are routinely used 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 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 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, paints also protect the surface from the surrounding elements and prevent or reduce the corrosive process.

[0002] Paints and coatings, while protecting the substrate from external environment, can themselves get dirty over time. The dirt can dull the coating by increasing the light scattering or by modifying the color of the coating. Dirt can also affect a paint's durability. Thus, it is desirable to have coatings with a hydrophilic surface and self-cleaning properties. A hydrophilic surface would allow water to spread out in a thin layer, sweeping dirt off the surface as the water thins out and trickles away. This type of "self-cleaning" behavior is advantageous to an exterior paint, as it keeps the coating clean without requiring extensive cleaning by the customer. A hydrophilic surface would allow water to sheathe over the surface and either solvate or even carry away the dirt molecules.

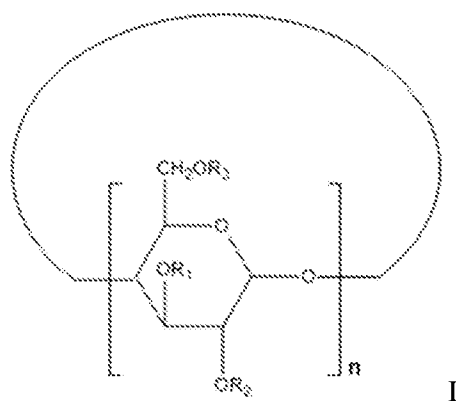
SUMMARY

[0003] The current disclosure is directed to paints and coatings with hydrophilic and self-cleaning properties. In one embodiment, a cyclodextrin compound is of formula I:



wherein each R_1 and each R_2 is, independently, H or a hydrophobic group, wherein at least one R_1 and at least one R_2 is a hydrophobic group; wherein each R_3 is independently, a hydrophilic group or H, wherein at least one R_3 is a hydrophilic group; and n is 6, 7, or 8.

[0004] In another embodiment, the cyclodextrin compound is of formula I:

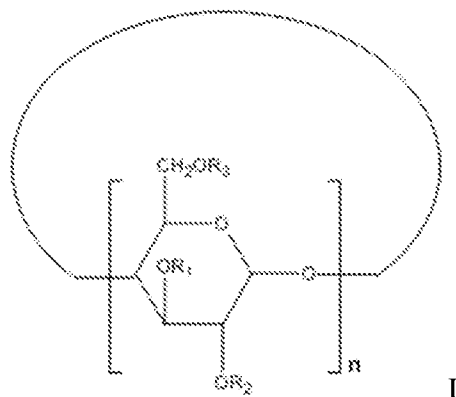


wherein each R_1 and each R_2 is, independently, H or a hydrophilic group, and at least one R_1 and at least one R_2 is a hydrophilic group; each R_3 is independently, a hydrophobic group or H, wherein at least one R_3 is a hydrophobic group; and n is 6, 7, or 8.

[0005] In an additional embodiment, a method of making a cyclodextrin compound includes: (a) replacing a hydrogen atom of at least one primary hydroxyl group of cyclodextrin with a sterically bulky moiety to form a first protected cyclodextrin; (b) replacing a hydrogen atom of at least one secondary hydroxyl group of the first protected cyclodextrin with a hydrophobic group to form a second protected cyclodextrin; (c) removing at least one sterically bulky moiety from the second protected cyclodextrin to form a

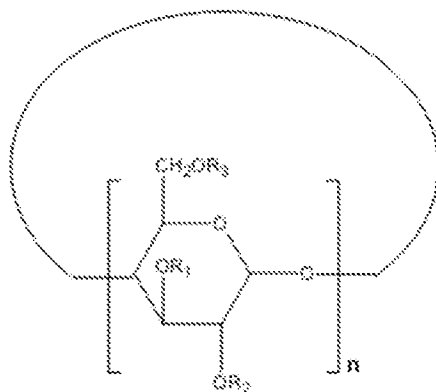
cyclodextrin having hydrophobic groups and free primary hydroxyl groups; and (d) replacing a hydrogen atom of at least one primary hydroxyl group of the cyclodextrin having hydrophobic groups with a hydrophilic group to form the cyclodextrin compound.

[0006] In a further embodiment, a hydrophilic coating composition may include a coating additive, wherein the additive is at least one cyclodextrin compound having the formula I:



wherein each R1 and each R2 is, independently, H or a hydrophobic group, and at least one R1 and at least one R2 is a hydrophobic group; each R3 is, independently, a hydrophilic group or H, wherein at least one R3 is a hydrophilic group; and n is 6, 7, or 8.

[0007] In another embodiment, a method of coating a substrate may involve applying a coating composition to the substrate, wherein the coating composition includes at least one cyclodextrin compound of formula I



wherein each R_1 and each R_2 is, independently, H or a hydrophobic group, and at least one R_1 and at least one R_2 is a hydrophobic group; each R_3 is, independently, a hydrophilic group or H, wherein at least one R_3 is a hydrophilic group; and n is 6, 7, or 8.

BRIEF DESCRIPTION OF THE FIGURE

[0008] FIG. 1 illustrates the preparation of an amphiphilic cyclodextrin according to an embodiment.

DETAILED DESCRIPTION

[0009] 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.

[0010] “Amphiphilic” means a three-dimensional structure having discrete hydrophobic and hydrophilic regions. An amphiphilic compound has the presence of both hydrophobic and hydrophilic elements.

[0011] “Alkyl” refers to monovalent saturated aliphatic hydrocarbyl groups having from 1 to 24 carbon atoms or 1 to 10 carbon atoms. This term includes, by way of example, linear and branched hydrocarbyl groups such as methyl ($-\text{CH}_3$), ethyl ($-\text{CH}_2\text{CH}_3$), n-propyl ($-\text{CH}_2\text{CH}_2\text{CH}_3$), isopropyl ($((\text{CH}_3)_2\text{CH}-)$), n-butyl ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$), isobutyl ($((\text{CH}_3)_2\text{CHCH}_2-$), sec-butyl ($((\text{CH}_3)(\text{CH}_3\text{CH}_2)\text{CH}-)$, and t-butyl ($((\text{CH}_3)_3\text{C}-)$.

[0012] “Alkenyl” means a straight or branched alkyl group having one or more double carbon-carbon bonds and 2-24 carbon atoms, including, but not limited to, ethenyl, 1-propenyl, 2-propenyl, 2-methyl-1-propenyl, 1-butenyl, 2-butenyl, and the like. In some embodiments, the alkenyl chain is 2 to 10 carbon atoms in length, 2 to 8 carbon atoms in length, 2 to 6 carbon atoms in length, or 2 to 4 carbon atoms in length.

[0013] “Alkynyl” refers to a straight or branched alkyl group having one or more triple carbon-carbon bonds and 2-20 carbon atoms, including, but not limited to, acetylene, 1-propylene, 2-propylene, and the like. In some embodiments, the alkynyl chain is 2 to 10 carbon atoms in length, 2 to 8 carbon atoms in length, 2 to 6 carbon atoms in length, or 2 to 4 carbon atoms in length.

[0014] “Aryl” refers to an aromatic carbocyclic group from 5 to 14 carbon atoms having a single ring (e.g., benzo) or multiple condensed rings (e.g., naphthyl, biphenyl or anthryl) which condensed rings may or may not be aromatic.

[0015] “Haloalkyl” refers to alkyl groups in which one or more hydrogen atoms are replaced by one or more chlorine, fluorine, bromine, iodine atoms, or any combination thereof.

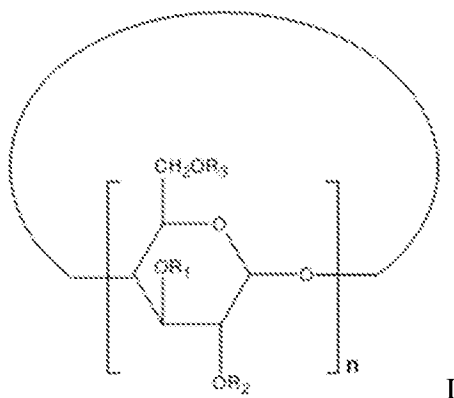
[0016] “Cycloalkyl” refers to non-aromatic cyclic hydrocarbons including cyclized alkyl, alkenyl, and alkynyl groups that contain up to 20 ring-forming carbon atoms. Cycloalkyl groups can include mono- or polycyclic ring systems such as fused ring systems, bridged ring systems, and spiro ring systems. In some embodiments, polycyclic ring systems include 2, 3, or 4 fused rings. A cycloalkyl group can contain 3 to 15, 3 to 10, 3 to 8, 3 to 6, 4 to 6, 3 to 5, or 5 or 6 ring-forming carbon atoms. Ring-forming carbon atoms of a cycloalkyl group can be optionally substituted by oxo or sulfido. Examples of cycloalkyl groups include, but are not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclopentenyl, cyclohexenyl, cyclohexadienyl, cycloheptatrienyl, norbornyl, norpinyl, norcarnyl, adamantyl, and the like.

[0017] As paints and coatings become covered and contaminated with unwanted substances, the appearance of the object often changes in undesirable ways. It is often expensive, time consuming, and sometimes hazardous to clean the coated surface, and the detergents, surfactants, fragrances, alkali, lime, and/or other chemicals used to clean the

surface make their way into the environment where they can potentially cause damage. Thus, it is desirable to have a coating with a hydrophilic surface that keeps dirt from sticking to the surface, is self-cleaning, and contains environmental friendly chemicals.

[0018] Cyclodextrins are a group of cyclic oligosaccharides in which glucopyranosyl residues are joined by alpha (1 to 4) glycoside linkages. Three attractive cyclodextrins are alpha, beta and gamma cyclodextrins, which have, respectively, six, seven and eight glucopyranosyl residues. Topographically, the cyclodextrins may be represented as a torus, the upper rim of which is lined with primary hydroxyl groups, and the lower rim with secondary hydroxyl groups. Coaxially aligned with the torus is a channel-like cavity of about 5, 6 or 7.5 angstrom units in diameter for the alpha, beta and gamma cyclodextrins, respectively. Since each of the glucopyranosyl residues has two secondary hydroxyl groups and one primary hydroxyl group, the alpha, beta and gamma cyclodextrins have, respectively, 18, 21 or 24 hydroxyl groups that can be modified.

[0019] In some embodiments, the cyclodextrin can be of formula I:

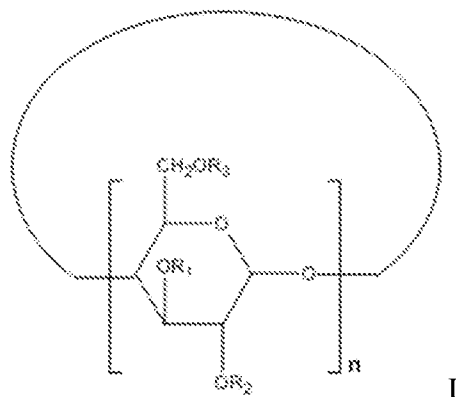


wherein each R_1 and each R_2 is, independently, H or a hydrophobic group, and at least one R_1 and at least one R_2 is a hydrophobic group; each R_3 is, independently, a hydrophilic group or H, wherein at least one R_3 is a hydrophilic group; and n is 6, 7, or 8.

[0020] Examples of hydrophilic groups include, but are not limited to, polyethylene glycol, amine, amide, epoxide, lactone, carboxyl, or carbonyl. The polyethylene

glycol may be methyl-capped and is represented by the formula $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n-$, wherein n is an integer of 2 to 24. The hydrophobic groups that are attached to the cyclodextrin may be, but are not limited to, alkyl, alkenyl, alkynyl, haloalkyl, cycloalkyl, or aryl groups. The presence of hydrophilic groups on the upper rim and the hydrophobic groups on the lower rim creates an amphiphilic cyclodextrin molecule.

[0021] In some embodiments, the cyclodextrin is of formula I:



wherein each R_1 and each R_2 is, independently, H or a hydrophilic group, and at least one R_1 and at least one R_2 is a hydrophilic group; wherein each R_3 is, independently, a hydrophobic group or H, wherein at least one R_3 is a hydrophobic group; and n is 6, 7, or 8.

[0022] In some embodiments, the alpha cyclodextrin may have the following substitutions: R_1 is $-(\text{CH}_2)_{20}-\text{CH}_3$, R_2 is $-(\text{CH}_2)_{20}-\text{CH}_3$, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10}-$; R_1 is alkyl, R_2 is alkyl, and R_3 is amine; R_1 is alkyl, R_2 is alkyl, and R_3 is epoxide; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is lactone; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is a carboxyl group; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20}-$; R_1 is haloalkyl, R_2 is cycloalkyl, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20}-$; R_1 is haloalkyl, R_2 is haloalkyl, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20}-$; R_1 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10}-$, R_2 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10}-$, and R_3 is $-(\text{CH}_2)_{20}-\text{CH}_3$ or R_1 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20}-$, R_2 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20}-$, and R_3 is $-(\text{CH}_2)_{20}-\text{CH}_3$.

[0023] In some embodiments, the beta cyclodextrin may have the following substitutions: R_1 is $-(\text{CH}_2)_{20}-\text{CH}_3$, R_2 is $-(\text{CH}_2)_{20}-\text{CH}_3$, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10}-$; R_1 is

alkyl, R_2 is alkyl, and R_3 is amine; R_1 is alkyl, R_2 is alkyl, and R_3 is epoxide; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is lactone; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is a carboxyl group; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20-}$; R_1 is haloalkyl, R_2 is cycloalkyl, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20-}$; R_1 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10-}$, R_2 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10-}$, and R_3 is $-(\text{CH}_2)_{20}-\text{CH}_3$ or R_1 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20-}$, R_2 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20-}$, and R_3 is $-(\text{CH}_2)_{20}-\text{CH}_3$.

[0024] In some embodiments, the gamma cyclodextrin may have the following substitutions: R_1 is $-(\text{CH}_2)_{20}-\text{CH}_3$, R_2 is $-(\text{CH}_2)_{20}-\text{CH}_3$, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10-}$; R_1 is alkyl, R_2 is alkyl, and R_3 is amine; R_1 is alkyl, R_2 is alkyl, and R_3 is epoxide; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is lactone; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is a carboxyl group; R_1 is alkyl, R_2 is cycloalkyl, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20-}$; R_1 is haloalkyl, R_2 is cycloalkyl, and R_3 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20-}$; R_1 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10-}$, R_2 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{10-}$, and R_3 is $-(\text{CH}_2)_{20}-\text{CH}_3$ or R_1 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20-}$, R_2 is $\text{CH}_3(\text{OCH}_2\text{CH}_2)_{20-}$, and R_3 is $-(\text{CH}_2)_{20}-\text{CH}_3$.

[0025] In some embodiments, a method of making a cyclodextrin compound may involve: (a) replacing a hydrogen atom of at least one primary hydroxyl group of cyclodextrin with a sterically bulky moiety to form a first protected cyclodextrin; (b) replacing a hydrogen atom of at least one secondary hydroxyl group of the first protected cyclodextrin with a hydrophobic group to form a second protected cyclodextrin; (c) removing at least one sterically bulky moiety from the second protected cyclodextrin to form a cyclodextrin having hydrophobic groups and free primary hydroxyl groups; and (d) replacing a hydrogen atom of at least one primary hydroxyl group of the cyclodextrin having hydrophobic groups with a hydrophilic group to form the cyclodextrin compound. Representative reaction steps are outlined in FIG.1.

[0026] The first step of the reaction can include protecting one or more primary hydroxyl groups of the cyclodextrin with a sterically bulky moiety to form a first protected cyclodextrin. This may be performed by contacting the cyclodextrin with a sterically bulky moiety in the presence of a base. Cyclodextrins used for this modification may be alpha, beta or gamma cyclodextrins. Further, a number of sterically bulky moieties, such as trityl, tert-butyl dimethylsilyl, trimethylsilyl, triisopropylsilyl, or tosyl groups may be used in this step. Examples of trityl groups that may be used are trityl halide, dimethoxy trityl halide, and methoxy trityl halide. The base catalyst may be a pyridine or any non-nucleophilic amine. This reaction step may be performed at a temperature of about 70 °C to about 90 °C, of about 70 °C to about 85 °C, of about 70 °C to about 80 °C, or of about 70 °C to about 75 °C. Examples of specific temperatures also include about 70 °C, about 75 °C, about 80 °C, about 85 °C, about 90 °C, and ranges between any two of these values (and including the endpoints). One purpose of blocking the primary hydroxyl groups is to protect these groups from the subsequent reaction with the alkyl halides, thus forcing the alkyl halides to react with secondary alcohol groups and not the primary alcohols.

[0027] Another step of the reaction can include replacing one or more hydrogen atoms of at least one secondary alcohol group of the first protected cyclodextrin. This reaction may be performed by contacting the first protected cyclodextrin with any of the following: an alkyl halide, a tosylate or a mesylate, in the presence of an alkali metal hydride or an alkaline earth metal hydride. Examples of alkali metal hydrides include sodium hydride, potassium hydride, lithium hydride and the like. Examples of alkaline earth metal hydride include, but are not limited to, magnesium hydride and calcium hydride. The alkyl halide used in the reaction may be an alkyl bromide, an alkyl chloride, an alkyl iodide or an alkyl fluoride, with the length of C atoms from 2 to 24. This reaction may be performed at room temperature for about 30 minutes to about 4 hours, for about 30 minutes to about 2 hours, or

for about 30 minutes to about 1 hour. Specific examples of times also include about 30 minutes, about 1 hour, about 1.5 hours, about 2 hours, about 3 hours, about 4 hours, and ranges between any two of these values (including the end points). This reaction results in the formation of a second protected cyclodextrin, with one or more sterically bulky moieties replacing one or more primary hydroxyl groups, and one or more alkyl groups in the place of secondary hydroxyl groups.

[0028] Another step can include removing at least one sterically bulky moiety. This may be performed by reacting the cyclodextrin obtained from the previously mentioned step with an acid, such as fluoroboric acid or trifluoroacetic acid. A solvent mixture of any of the following may be used in this step: dichloromethane, ethyl acetate, chloroform, dimethylformamide, propanol, ethanol, butanol, methanol or combinations thereof. This reaction results in formation of one or more free primary hydroxyl groups, which can be replaced with one or more hydrophobic groups.

[0029] Another step of the reaction can include replacing one or more of the primary hydroxyl groups of the cyclodextrin obtained from the previous step, with one or more hydrophilic groups. This step may be carried out by, for example, a Mitsunobu coupling reaction, which is well known in the art. Typically, the Mitsunobu reaction involves conversion of one or more of the hydroxyl groups into a potent leaving group that is able to be displaced by a wide variety of nucleophiles. In addition, a modified Mitsunobu reaction may also be used, as this helps in simplifying the separation of the desired product, and avoiding the production of undesired by-products. This step of the reaction may be performed by using triphenylphosphine in combination with diethyl azodicarboxylate (DEAD), diisopropyl azodicarboxylate (DIAD), dibenzyl azodicarboxylate (DBAB) or di-(4-chlorobenzyl) azodicarboxylate (DCAD). Modified Mitsunobu catalysts such as tri-*n*-butylphosphine in combination with *N,N,N',N'*-tetramethylazodicarboxamide or 1,1'-

(azodicarbonyl) dipiperidine may also be used. In some reactions, cyanomethylenetri-n-butylphosphorane alone can replace both triphenylphosphine and DEAD. Such a reaction would result in the formation of cyclodextrins with hydrophilic groups occupying at least one primary alcohol position, and hydrophobic groups occupying at least one secondary alcohol position.

[0030] The amphiphilic cyclodextrins disclosed herein may be incorporated in paints and coatings, providing a hydrophilic property to the paints. The hydrophobic side of the cyclodextrin may mix well with curing latex paint, thus becoming partially or fully trapped in the paint particles. The hydrophilic portion of the cyclodextrin would remain free to decorate the surface and the hydrophilic side-chains “fan out”, forming a water-loving layer over the underlying acrylic surface. The extensive ether linkages present in the polyethylene glycol groups would be free to interact heavily with the water molecule, thus forming a hydrophilic surface.

[0031] The cyclodextrin additives disclosed herein may be dispersed in one or more organic binders, such as a polymeric organic binder. 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, for example, 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 also include a single binder or a mixture of two or more polymeric binders that may be of the same class or different classes. For example, organic binders may be combined with a silicon-based binder.

[0032] In some embodiments, the cyclodextrin additives 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.

[0033] The cyclodextrin additives may be added to a paint composition during any step of the paint preparation or before a consumer uses the paint. The cyclodextrin additives may be present as a separate component or a kit, and mixed with the paint before use. For example, the end consumer may add the cyclodextrin additive to any conventional paint formulation before use.

[0034] The cyclodextrin additives may be present in a paint formulation at about 0.5 to about 40 weight percent, at about 0.5 to about 20 weight percent, at about 0.5 to about 10 weight percent, at about 0.5 to about 5 weight percent, or at about 0.5 to about 1 weight percent. Additional specific examples include about 0.5 weight percent, about 0.7 weight percent, about 1 weight percent, about 2 weight percent, about 5 weight percent, about 10 weight percent, about 15 weight percent, about 30 weight percent, about 40 weight percent of the total weight, and ranges between any two of these values (including the endpoints).

[0035] Paints and coatings may contain one or more additives in their composition. These additives may alter one or more of the properties of the paint, such as shelf life, application, 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, but are not limited to, initiators, rheology modifiers, preservatives, coalescing agents, and the like. Initiators are a source of free radicals to initiate the polymerization process in which monomers condense to form the polymers. Coatings may contain a redox system initiator, such as ferrous and thiosulfate salts along with the persulfate salts, that promote polymerization at room temperature.

[0036] Thickeners and rheology modifiers may be also be added to coatings to achieve the desired viscosity and flow properties. Thickeners function by, for example, 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.

[0037] 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.

[0038] 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, ensure film formation under varying atmospheric conditions. They may be slow evaporating solvents with some solubility in the polymer phase. They may also act as a temporary plasticizer, allowing film formation at temperatures below the system's glass transition temperature. After film formation, the coalescing agents may slowly diffuse to the surface and evaporate, increasing the hardness and block resistance of the film.

[0039] Coatings may further contain one or more of the following additives: 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. Both ionic and non-ionic surfactants may be used. Examples may include, but are not limited to, alkyl phenol ethoxylates, sodium lauryl sulfate, dodecylbenzene sulfonate, polyoxyethylene alkyl ethers, polyoxyethylene alkyl allyl ethers, acetylene glycols, polyoxyethylene, stearic acid and polyoxypropylene.

[0040] One or more plasticizers may be added to the compositions to adjust the tensile properties of the paint film. Plasticizers include, for example, a glucose-based

derivative, a glycerine-based derivative, propylene glycol, ethylene glycol, phthalates and the like.

[0041] Paints may further include one or more pigments. The term “pigments” is intended to embrace, without limitation, pigmentary compounds employed as colorants, including white pigments, as well as ingredients commonly known in the art as “opacifying agents” and “fillers”. Pigments may be any particulate organic or inorganic compound and may provide coatings the ability to obscure a background of contrasting color (hiding power).

[0042] The coating of the present disclosure may be a decorative coating, an industrial coating, a protective coating, or a self-cleaning coating, or any combination thereof. The 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, exemplary substrates include, an exterior of a building, vehicles, bridges, airplanes, metal railings, fence, 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.

[0043] One function of an exemplary coating embodiment may be summarized as follows: during the curing of the paint, the hydrophobic side chains of the cyclodextrins may easily become entrapped /embedded in the cured hydrophobic latex acrylic. As the paint cures and the water solvent evaporates, the latex particles may fuse together to form the finished paint, with the hydrophilic end of the cyclodextrin “brushing” out from the surface of the paint surface. This hydrophilic region on the surface of the paint allows the incoming water droplets to spread out and prevent beading, promoting a “self-cleaning” action. The resulting paint may keep painted objects clean with little external maintenance, by relying on the force generated by natural rainfall or by simple rinsing with water. Exterior surfaces such

as buildings and monuments which are currently difficult to maintain will especially benefit from this technology and save maintenance costs.

EXAMPLES

EXAMPLE 1: Preparation of modified cyclodextrin

[0044] Step 1: Anhydrous beta cyclodextrin (5.00 g, 4.41 mmol) is dissolved in 40 ml of dry pyridine. To this solution, trityl chloride (8.60 g, 30.8 mmol) is added and the mixture is stirred at 80 °C for 24 hours. The reaction is continued for 9 days with the addition of trityl chloride (1.08 g, 4.41 mmol) each day. The total amount of trityl chloride added is 70.5 mmol (16.0 equivalents). At the end of this period, the product formed is analyzed by a thin-layer chromatography ($R_f = 0.32$, dichloromethane : methanol : water ratio 85 : 15 : 1.5). The reaction mixture is then added slowly to 1000 mL of water with stirring, resulting in immediate precipitation of a solid. The precipitate is collected by filtration, washed twice with 200 mL water (each time), and dried under vacuum. The resulting product is per-6-*O*-triphenylmethyl-beta-cyclodextrin.

[0045] Step 2: The above product (1.03 g, 0.36 mmol) is dissolved in anhydrous dimethyl formamide (10 mL). To this solution, sodium hydride (60% dispersion in mineral oil, 407 mg, 10.2 mmol) is added slowly, and the mixture is stirred at room temperature for five minutes. At the end of this period, the mixture is cooled to 0 °C using an ice bath. To this cold solution, 1-bromoheptadecane (2.41 g, 7.56 mmol) is added dropwise. The reaction is continued for 3 hours with constant stirring, followed by addition of methanol (3 mL) to quench the unreacted sodium hydride. The reaction mixture is then diluted with water (100 mL), and the mixture is extracted with ethyl acetate (100 mL). The organic solution is dried over anhydrous magnesium sulfate, and the solvent is evaporated under reduced pressure. The product obtained is a protected /alkylated beta-cyclodextrin.

[0046] Step 3: About 1 mmol of the above product is dissolved in a 2:1 mixture of dichloromethane-methanol (25 mL). The mixture is stirred at room temperature, and an aqueous solution of 50% fluoroboric acid is added dropwise over 30 minutes. The reaction mixture is further stirred at room temperature for three hours, and at the end of this period the pH of the mixture is measured, and if required, adjusted to between 7 and 8 by adding few drops of concentrated ammonium hydroxide. The solution is then evaporated under reduced pressure, and the residue is recrystallized.

[0047] Step 4: The final step of the reaction is carried out by the Mitsunobu coupling step, by using a slight stoichiometric excess (1.05 moles per mole of alcohol group being substituted) of triphenylphosphine and DEAD dissolved in dry dichloromethane at 0 °C. With continued stirring, an equimolar amount of the mono-functional (alkyl-capped) polyethylene glycol oligomer is added dropwise to the above mixture. This is followed by addition of cyclodextrin product from step 3 dissolved in dry dichloromethane. The temperature of the reaction is maintained at 0 °C throughout the period, with constant stirring. At the end of 2 hours, the reaction mixture is allowed to warm to room temperature, and the mixture is quenched by the addition of ethanol. The alcohol layer containing the desired product is decanted away from the precipitated solids, and flushed through a small filter pad of silica gel using ethanol as the eluent. The combined alcohol fractions are then evaporated under reduced pressure to yield beta cyclodextrin with heptadecane groups occupying the secondary hydroxyl positions, and polyethylene glycol groups occupying the primary hydroxyl positions.

EXAMPLE 2: Preparation of a hydrophilic coating containing a cyclodextrin

[0048] A hydrophilic coating is prepared having the following components: 40 grams of chromium oxide pigment, 2 grams of cyclodextrin compound (from Example 1), 2 grams of thickener (hydroxyethyl cellulose), 150 grams of solvent (water), 70 grams of

binder (methyl methacrylate), 0.3 grams of coalescing agent (2,2,4-trimethyl-1,3-pentanediolmono(2-methylpropanoate)), and 0.05 grams of bactericide. The components are mixed under high shear for 30 minutes.

EXAMPLE 3: Preparation of a hydrophilic coating without cyclodextrin

[0049] A hydrophilic coating is prepared having the following components: 40 grams of chromium oxide pigment, 2 grams of thickener (hydroxyethyl cellulose), 150 grams of solvent (water), 70 grams of binder (methyl methacrylate), 0.3 grams of coalescing agent (2,2,4-trimethyl-1,3-pentanediolmono(2-methylpropanoate)), and 0.05 grams of bactericide. The components are mixed under high shear for 30 minutes.

EXAMPLE 4: Evaluation of hydrophilic property

[0050] The hydrophilic coating of Example 2 is coated on a glass surface and dried at room temperature. The surface free energy and the water droplet contact angle of the hydrophilic coating is measured as follows. A Zisman plotting method is employed for measuring the surface free energy. The surface tension of various concentrations of the aqueous solution of magnesium chloride is plotted along the X-axis, and the contact angle in terms of $\cos \theta$ is plotted along the Y-axis. A graph with a linear relationship between the two is obtained. The graph is extrapolated such that the surface tension at contact angle 0° is measured and is defined as the surface free energy of the solid. The surface free energy of the glass surface measured will be 85 milliNewton/meter.

EXAMPLE 5: An object coated with hydrophilic paint

[0051] A metal table is painted with a hydrophilic coating containing cyclodextrin additives (Example 1) and is allowed to dry at room temperature. The surface free energy of the chair is measured as explained in Example 4 and will be 85 milliNewton /meter. The anti-fouling property of the coating is measured as follows: A line is drawn on the above

mentioned coated table using oily ink. A similar line is also drawn on a table which is coated with a paint without cyclodextrin (Example 3). An uncoated table is also used in this experiment. A water jet is continuously applied on all the three surfaces and periodically checked whether the oily line is erased. The oily ink applied on the coated table will be erased after 1 minute, whereas the oily line on the un-coated table or on the table with a paint lacking cyclodextrin will be un-changed and visible.

EXAMPLE 6: Anti-fouling properties

[0052] The procedure involves three concrete surfaces, coating one concrete surface with a hydrophilic paint with cyclodextrin additives (Example 1), coating the second concrete surface with a paint without cyclodextrins (Example 3), and the third concrete surface without any coating. After drying the paint, all the three surfaces are exposed to running water for one month. At the end of the period, the concrete surface is checked for visible peeling of the paint and growth of organisms such as algae. The concrete surface coated with the hydrophilic paint containing cyclodextrins will be clear of microorganisms and algae, whereas the other two concrete surfaces will exhibit the growth of microorganisms.

[0053] 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.

[0054] 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.

[0055] 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.”

[0056] 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.

[0057] 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.

[0058] 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.”

[0059] 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.

[0060] 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

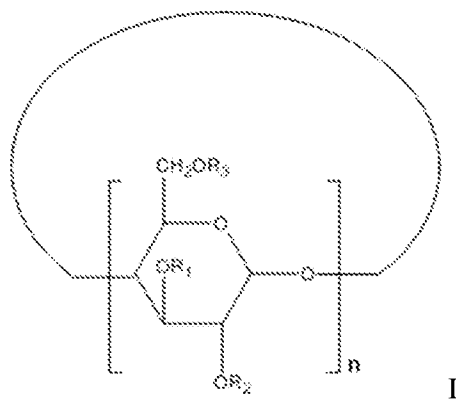
third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled 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.

[0061] 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 cyclodextrin compound of formula I:



wherein:

each R1 is, independently, a hydrophobic group or H, wherein at least one R1 is a hydrophobic group;

each R2 is, independently, a hydrophobic group or H, wherein at least one R2 is a hydrophobic group;

each R3 is, independently, a hydrophilic group or H, wherein at least one R3 is a hydrophilic group; and

n is 6, 7, or 8.

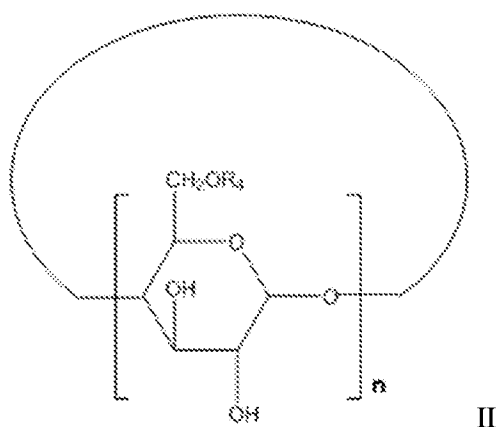
2. The compound of claim 1, wherein each hydrophobic group is, independently, alkyl, alkenyl, alkynyl, haloalkyl, cycloalkyl, or aryl.

3. The compound of claim 1, wherein each hydrophilic group is, independently, polyethylene glycol, methyl-polyethylene glycol, amine, amide, epoxide, lactone, carboxyl, or carbonyl.

4. The compound of claim 1, wherein each R1 is alkyl or haloalkyl.

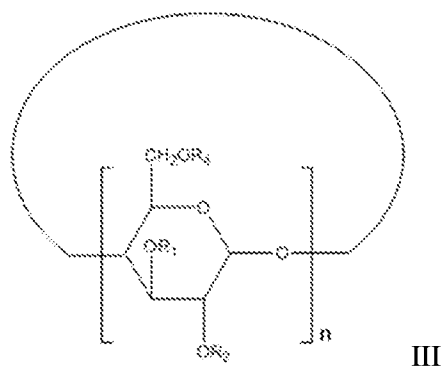
5. The compound of claim 1, wherein each R_2 is alkyl or haloalkyl.
6. The compound of claim 1, wherein each R_3 is methyl-polyethylene glycol or epoxide.
7. The compound of claim 1, wherein each R_1 is $-(CH_2)_{20}-CH_3$, each R_2 is $-(CH_2)_{20}-CH_3$ and each R_3 is $-(CH_2CH_2O)_{20}CH_3$.
8. A method of making a cyclodextrin compound, the method comprising:

replacing a hydrogen atom of at least one primary hydroxyl group of cyclodextrin with R_4 to form a first protected cyclodextrin, which is represented by formula II:



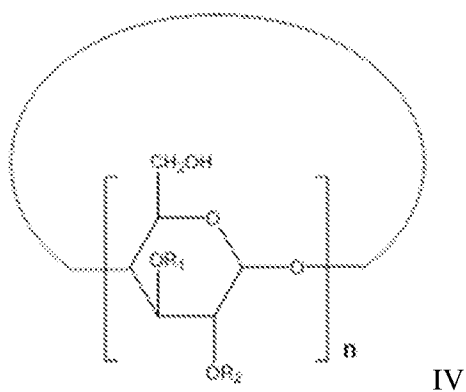
wherein each R_4 is, independently, H or a sterically bulky moiety, and at least one R_4 is a sterically bulky moiety; and n is 6, 7, or 8;

replacing a hydrogen atom of at least one secondary hydroxyl group of the first protected cyclodextrin with R_1 and R_2 to form a second protected cyclodextrin, which is represented by formula III:



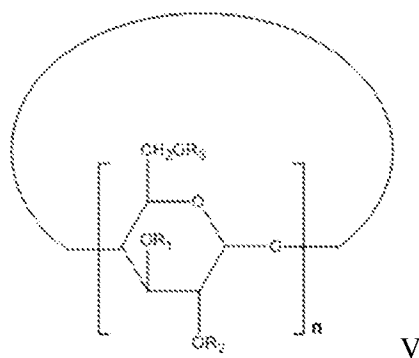
wherein each R1 and each R2 is, independently, H or a hydrophobic group, and at least one R1 and at least one R2 is a hydrophobic group;

removing at least one sterically bulky moiety from the second protected cyclodextrin to form a cyclodextrin having hydrophobic groups and free primary hydroxyl groups, which is represented by formula IV:



and

replacing a hydrogen atom of at least one primary hydroxyl group of the cyclodextrin having hydrophobic groups with R3 to form the cyclodextrin compound, which is represented by formula V:



wherein each R₃ is independently, H or a hydrophilic group, wherein at least one R₃ is a hydrophilic group.

9. The method of claim 8, wherein the cyclodextrin of formula V is alpha cyclodextrin, beta cyclodextrin, or gamma cyclodextrin.

10. The method of claim 8, wherein each sterically bulky moiety is, independently, a trityl, tert-butyldimethylsilyl, trimethylsilyl, triisopropylsilyl, or tosyl group.

11. The method of claim 8, wherein each sterically bulky moiety is, independently, trityl halide, dimethoxy trityl halide, or methoxy trityl halide.

12. The method of claim 8, wherein each hydrophobic group is, independently, alkyl, alkenyl, alkynyl, haloalkyl, cycloalkyl, or aryl.

13. The method of claim 8, wherein each hydrophilic group is, independently, a polyethylene glycol, methyl-polyethylene glycol, an amine, an amide, an epoxide, a lactone, a carboxyl, or a carbonyl.

14. The method of claim 8, wherein replacing a hydrogen atom of at least one primary hydroxyl group of cyclodextrin comprises contacting the cyclodextrin with the sterically bulky moiety in the presence of a base.

15. The method of claim 14, wherein the base is a pyridine.
16. The method of claim 14, wherein contacting cyclodextrin, the sterically bulky moiety, and the base is performed at a temperature of about 70 °C to about 90 °C.
17. The method of claim 8, wherein replacing a hydrogen atom of at least one secondary alcohol group of the first protected cyclodextrin comprises contacting the first protected cyclodextrin with an alkyl halide in the presence of a hydride.
18. The method of claim 17, wherein the alkyl halide has a chain length of 2 to 24 carbon atoms.
19. The method of claim 17, wherein the hydride is an alkali metal hydride or an alkaline earth metal hydride.
20. The method of claim 17, wherein contacting the first protected cyclodextrin, the alkyl halide, and the hydride is performed at room temperature.
21. The method of claim 17, wherein contacting the first protected cyclodextrin, the alkyl halide, and the hydride is performed for about 30 minutes to about 4 hours.
22. The method of claim 8, wherein removing the sterically bulky moiety from the second protected cyclodextrin comprises contacting the second protected cyclodextrin with an acid in the presence of a solvent.
23. The method of claim 22, wherein the acid is fluoroboric acid.
24. The method of claim 22, wherein the solvent is a mixture of dichloromethane and methanol.

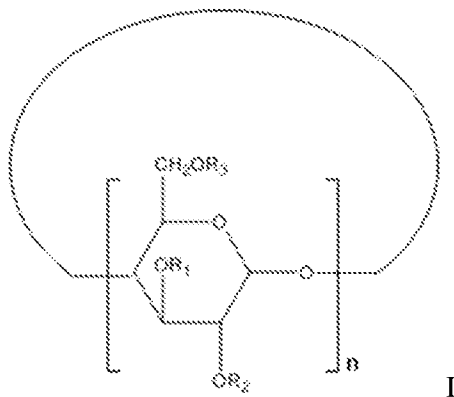
25. The method of claim 8, wherein replacing a hydrogen atom of at least one primary hydroxyl group of the cyclodextrin having hydrophobic groups and free primary hydroxyl groups with a hydrophilic group comprises contacting the hydrophilic group with the cyclodextrin having hydrophobic groups and free primary hydroxyl groups in the presence of an activating agent.

26. The method of claim 25, wherein the activating agent is diethyl azodicarboxylate, diisopropyl azodicarboxylate, di-(4-chlorobenzyl)azodicarboxylate, 1, 1'-(azodicarbonyl) dipiperidine, dibenzyl azodicarboxylate, N,N,N',N'-tetramethylazodicarboxamide, or cyanomethylenetri-n-butylphosphorane, or any combination thereof.

27. A hydrophilic coating composition comprising:

a coating additive which is at least one cyclodextrin compound having formula

I:



wherein:

each R1 is, independently, a hydrophobic group or H, wherein at least one R1 is a hydrophobic group;

each R2 is, independently, a hydrophobic group or H, wherein at least one R2 is a hydrophobic group;

each R3 is independently, a hydrophilic group or H, wherein at least one R3 is a hydrophilic group; and

n is 6, 7, or 8; and

at least one binder.

28. The composition of claim 27, wherein the binder comprises one or more silicone polymers or one or more organic polymers, or any combination thereof.

29. The composition of claim 27, wherein each hydrophobic group is, independently, alkyl, alkenyl, alkynyl, haloalkyl, cycloalkyl, or aryl.

30. The composition of claim 23, wherein each hydrophilic group is, independently, a polyethylene glycol, methyl-polyethylene glycol, an amide, an epoxide, a lactone, an amine, a carboxyl, or a carbonyl.

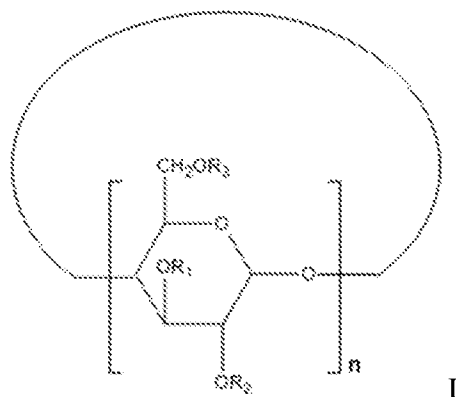
31. The composition of claim 27, wherein the cyclodextrin compound is present in about 0.5 weight percent to about 40 weight percent of the total coating composition.

32. The composition of claim 27, further comprising one or more of the following: a solvent, a coalescing agent, a pigment, a rheology modifier, a plasticizer, and a surfactant.

33. The composition of claim 27, wherein the coating composition is a decorative coating, an industrial coating, a protective coating, or a self-cleaning coating, or any combination thereof.

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

applying a coating composition to the substrate, wherein the coating composition comprises at least one cyclodextrin compound of formula I:



wherein:

each R1 is, independently, a hydrophobic group or H, wherein at least one R1 is a hydrophobic group;

each R2 is independently, a hydrophobic group or H, wherein at least one R2 is a hydrophobic group;

each R3 is independently, a hydrophilic group or H, wherein at least one R3 is a hydrophilic group; and

n is 6, 7, or 8.

35. The method of claim 34, wherein each hydrophobic group is, independently, alkyl, alkenyl, alkynyl, haloalkyl, cycloalkyl, or aryl.

36. The method of claim 34, wherein each hydrophilic group is, independently, a polyethylene glycol, methyl-polyethylene glycol, an amine, an amide, an epoxide, a lactone, a carboxyl, or a carbonyl.

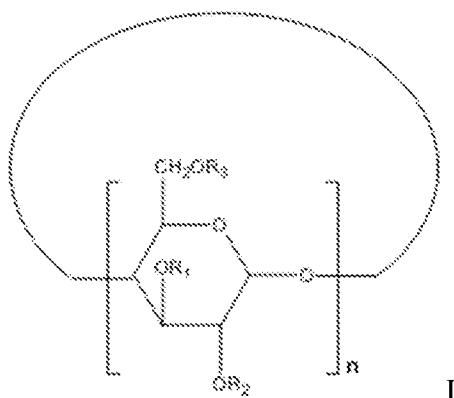
37. The method of claim 34, wherein the cyclodextrin derivative is present in about 0.5 weight percent to about 40 weight percent of the total coating composition.

38. The method of claim 34, wherein the coating composition further comprises one or more of the following: a binder, a solvent, a coalescing agent, a pigment, a rheology modifier, a plasticizer, and a surfactant.

39. The method of claim 34, wherein the coating composition is a decorative coating, an industrial coating, a protective coating, or a self-cleaning coating, or any combination thereof.

40. The method of claim 34, wherein the coating composition is applied to the substrate by coating, brushing, dipping, spraying, or rolling, or any combination thereof.

41. A cyclodextrin compound of formula I:



wherein:

each R1 is, independently, a hydrophilic group or H, wherein at least one R1 is a hydrophilic group;

each R2 is, independently, a hydrophilic group or H, wherein at least one R2 is a hydrophilic group;

each R3 is, independently, a hydrophobic group or H, and wherein at least one R3 is a hydrophobic group; and

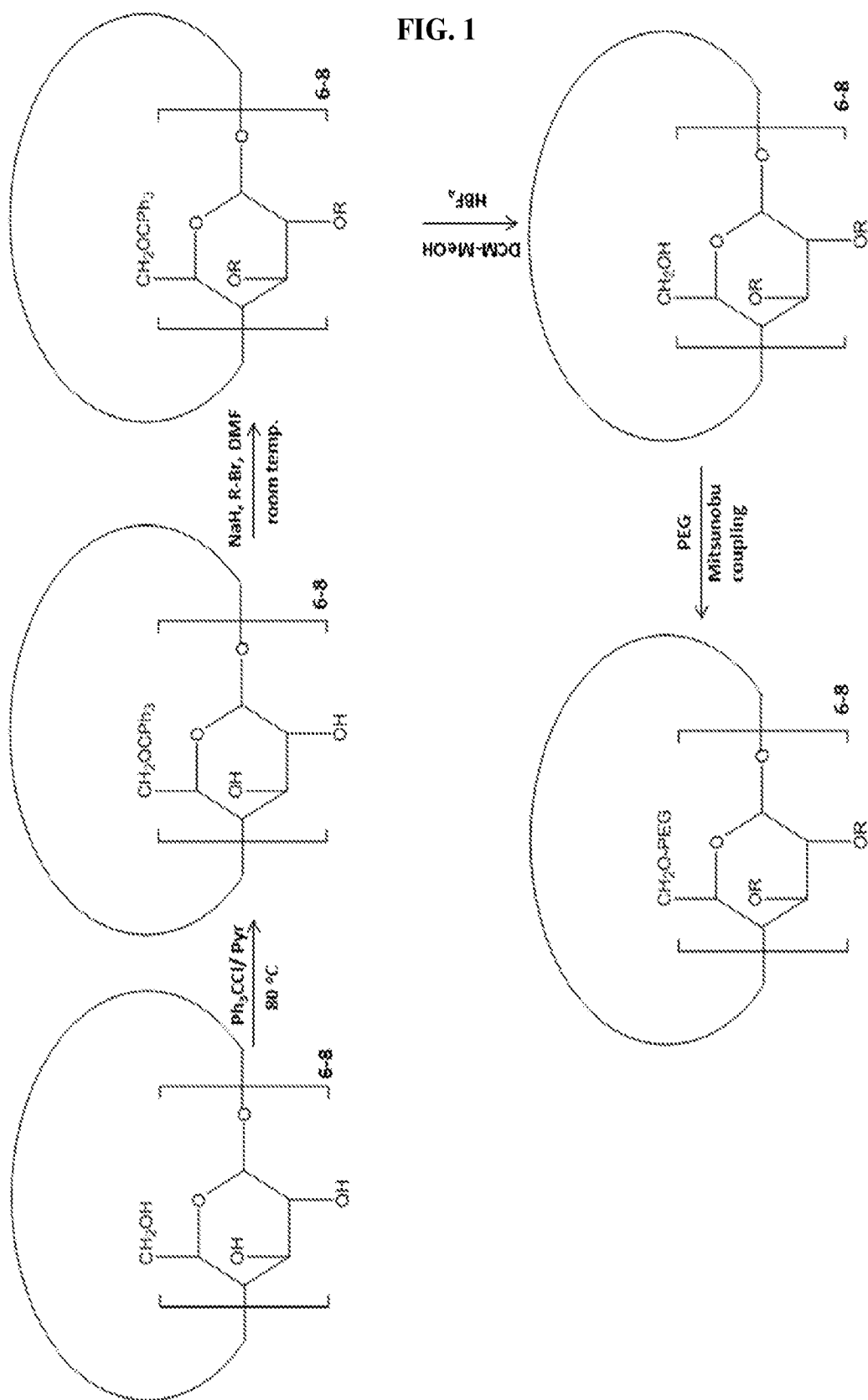
n is 6, 7, or 8.

42. The compound of claim 41, wherein each hydrophobic group is, independently, alkyl, alkenyl, alkynyl, haloalkyl, cycloalkyl, or aryl.

43. The compound of claim 41, wherein each hydrophilic group is, independently, polyethylene glycol, methyl-polyethylene glycol, an amine, an amide, an epoxide, a lactone, a carboxyl, or a carbonyl.

44. The compound of claim 41, wherein each R_1 is $-(CH_2CH_2O)_{20}CH_3$, each R_2 is $-(CH_2CH_2O)_{20}CH_3$ and each R_3 is $-(CH_2)_{20}-CH_3$.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/60046

A. CLASSIFICATION OF SUBJECT MATTER IPC(8) - A01N 43/04 (2013.01) USPC - 514/058 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) USPC: 514/058 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) Electronic Database Searched: THOMSON INNOVATION (US Grant, US App, EP Grant, EP App), SCIENCDIRECT, GOOGLE. Search Terms Used cyclodextrin hydrophilic hydrophobic, cyclodextrin hydrophilic, hydrophobic, substituent, glycol, amine		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,760,015 A (Joullie et al.) 02 June 1998 (02.06.1998) entire document especially figure 1, formula	1-7 and 41-44
Y	US 7,851,457 B2 (Hecht et al.) 14 December 2010 (14.10.2010) entire document especially figure 1	1-7 and 41-44
☐ 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 11 February 2013 (11.02.2013)		Date of mailing of the international search report 01 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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 12/60046

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:

---please see 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.:
1-7 and 41-44

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
Information on patent family members

International application No.
PCT/US 12/60046

LOU: BOX III continuation

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 1-7 and 41-44 directed towards cyclodextrin compound of formula I

Group II: claims 8-26 directed towards method of making a cyclodextrin compound, the method comprising: replacing a hydrogen atom of at least one primary hydroxyl group of cyclodextrin with R4 to form a first protected cyclodextrin, which is represented by formula II; replacing a hydrogen atom of at least one secondary hydroxyl group of the first protected cyclodextrin with R1 and R2 to form a second protected cyclodextrin, which is represented by formula III wherein each R1 and each R2 is, independently, H or a hydrophobic group, and at least one R1 and at least one R2 is a hydrophobic group; removing at least one sterically bulky moiety from the second protected cyclodextrin to form a cyclodextrin having hydrophobic groups and free primary hydroxyl groups, which is represented by formula IV and replacing a hydrogen atom of at least one primary hydroxyl group of the cyclodextrin having hydrophobic groups with R3 to form the cyclodextrin compound, which is represented by formula V: wherein each R3 is independently, H or a hydrophilic group, wherein at least one R3 is a hydrophilic group.

Group III: claims 27-40 directed towards hydrophilic coating composition comprising a coating additive which is at least one cyclodextrin compound having formula I

The inventions listed as Groups I-III 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 technical features for the following reasons:

The inventions of Group I-III share the technical feature of a cyclodextrin compound of formula which is disclosed by US 5,760,015 A to Joullie et al. (hereafter 'Joullie') in figure 1 (wherein R1, R2, R3 are H). Joullie further teaches at least one of R1, R2 or R3 are hydrophobic (see figure 5B, NH/SO4 group substituent). Therefore, the unity is lacking between Groups I-III under PCT Rule 13.