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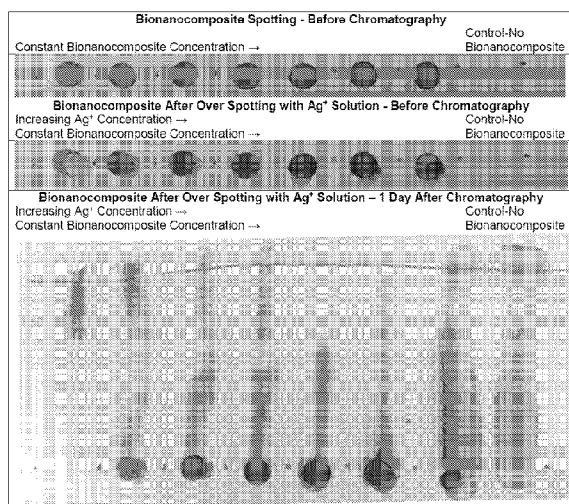


FIG. 1

(57) Abstract: Biocide-free antifouling and/or foul-releasing compositions that can be used alone or in coatings and paints are disclosed. The compositions are non-toxic, biodegradable and produced by ecofriendly reactions. In some embodiments, the compositions are regenerated by marine life secretions to regain their anti-fouling functionality after an initial sloughing cycle(s).



## **ANTI-FOULING AND FOUL-RELEASING COMPOSITIONS AND METHODS OF MAKING AND USING SAME**

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

**[0001]** This application claims the benefit of and priority to U.S. Provisional Patent Application No. 63/053,496, filed July 17, 2020, which is hereby incorporated by reference in its entirety.

### **STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH**

**[0002]** None.

### **BACKGROUND**

**[0003]** Currently, most paints used on ship hulls contain biocidal chemicals and/or heavy metals intentionally used to keep the ship hulls free of algae, mollusks, barnacles, and other marine life because biofouling decreases fuel efficiency and increases transport time and operating costs. While marine paints have various levels of efficacy, most are notorious ocean pollutants. As the paint sloughs off, in a process known as ablation or self-polishing, which is required for maintaining antifouling effectiveness, so do the harsh biocidal chemicals and metals. Over the decades, oceans have become increasingly polluted due to this sloughing process and general exposure to harmful marine paints. However, sustainability and the environment are now major regulatory drivers, and the paint industry must find ways to actively address these criteria.

### **SUMMARY**

**[0004]** The present disclosure generally relates to biocide-free antifouling and/or foul-releasing compositions and methods that can be used as coatings or paint additives. The compositions are non-toxic, biodegradable and produced by ecofriendly (e.g., water-based) reactions. Further, in some embodiments, the compositions are regenerated by marine life secretions to regain their anti-fouling and foul-releasing functionality after an initial sloughing cycle(s).

**[0005]** The disclosed compositions are engineered to contain at least three functional materials: a polyhydroxyaromatic polymer that creates an inhospitable attachment microenvironment at the substrate-water interface, a biopolymer that provides a sacrificial enzymatically labile fouling-release mechanism, and a crosslinking agent that tunes both the polymer network morphology and the material's binding affinity. In addition, an inorganic material may be used to provide mechanical stability and scaffolding.

**[0006]** In an aspect, an anti-fouling and/or foul-releasing composition comprises a crosslinked polyhydroxyaromatic polymer and a biopolymer at least partially encapsulated by the crosslinked polyhydroxyaromatic polymer.

**[0007]** In an embodiment, a polyhydroxyaromatic polymer comprises a plurality of hydroxyaromatic moieties. For example, a polyhydroxyaromatic polymer may be a polydihydroxyaromatic polymer, a polytrihydroxyaromatic polymer, or a polytetrahydroxyaromatic polymer. In an embodiment, a polyhydroxyaromatic polymer is a polyhydroxybenzene polymer, such as a polydihydroxybenzene polymer, a polytrihydroxybenzene polymer, or a polytetrahydroxybenzene polymer.

**[0008]** In an embodiment, monomers for forming a polyhydroxyaromatic polymer are selected from the group consisting of catechol, quinones, hydroquinones, dopamine, norepinephrine, epinephrine, catecholamines, catecholic amino acids, indoles, naphthalenes and combinations thereof. Generally, a monomer used to form a polyhydroxyaromatic polymer will contain at least one hydroxy moiety. Further, it will be understood that a polyhydroxyaromatic polymer may be linear, branched or a three-dimensional network formed when a monomer is also capable of acting as a crosslinking agent.

**[0009]** In an embodiment, a crosslinking agent for crosslinking polyhydroxyaromatic polymers is a monomer of the main polymer chain or is an independent monomer that does not exist in the main polymer chain. For example, an independent crosslinking agent for crosslinking polyhydroxyaromatic polymers may be selected from the group consisting of bifunctional alkanes, bifunctional amines, trifunctional amines, trifunctional silanes, thiol-based crosslinkers and combinations thereof. For example, the crosslinking agent may be a bifunctional

alkane (i.e., an alkane comprising two non-hydrogen substituents), a secondary amine (bifunctional amine) or tertiary amine (trifunctional amine) substituted with one or more substituents selected from the group consisting of linear or branched alkyl, alkenyl or alkynyl chains comprising between 0 and 24 carbon atoms where the chain (or central crosslinking atom when the substituent comprises 0 carbon atoms) is substituted with one or more amines, sulfhydryls, halogens, sulfonates, acrylates, silanes, silanols and selsesquioxanes. In some embodiments, when a substituent comprises an amine, the amine may be a diaminoalkyl, an aminoalkylthiol, an aminoalkylhalide, an aminoalkylsulfonate, an aminoalkylsilane/silanol, an aminoacrylate or an aminoalkylsilsesquioxane. In an embodiment, after crosslinking, amines within the crosslinked polyhydroxyaromatic polymer may be alkylated to produce tertiary or quaternary amines.

**[0010]** In an embodiment, a biopolymer is selected from the group consisting of double-stranded DNA (dsDNA), single-stranded DNA (ssDNA), serum albumins, hemoglobin, carbohydrates, saccharides and combinations thereof. In an embodiment, a biopolymer is antimicrobial and/or nucleophilic. In an embodiment, an anti-fouling composition disclosed herein comprises a biopolymer and/or a chelating agent, such as a porphyrin, a crown ether and combinations thereof.

**[0011]** In an embodiment, at least a portion of a biopolymer is cleaved from the anti-fouling composition by hydrolytic enzymes secreted by bacteria. In an embodiment, bacterial matter replaces at least a portion of the biopolymer cleaved from the anti-fouling composition, thereby self-healing and regenerating the anti-fouling composition.

**[0012]** In an embodiment, a concentration of the biopolymer is between 0.01% w/w and 99% w/w, or between 0.3% w/w and 75% w/w, or between 0.5% w/w and 50% w/w, or between 0.5% w/w and 25% w/w, or between 1% w/w and 15% w/w, or between 4% w/w and 12% w/w, or between 7% w/w and 10% w/w.

**[0013]** In an embodiment, at least a portion of the crosslinked polyhydroxyaromatic polymer and/or the biopolymer is bound to a metal or metal ion, such as an alkali metal, an alkaline earth metal, a transition metal, a lanthanide, an actinide, a rare earth metal or a metalloid. For example, the metal ion may be

selected from the group consisting of  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Pb}^{4+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cd}^+$ ,  $\text{Ag}^+$ ,  $\text{As}^{3+}$ ,  $\text{As}^{5+}$  and combinations thereof.

**[0014]** In an embodiment, an anti-fouling and/or foul-releasing composition further comprises a structural material, such as, but not limited to, a structural material selected from the group consisting of lignin, titanium dioxide, silica, bentonite clay, calcium carbonate, corals, zeolite, polyethyleneglycol (PEG) and combinations thereof.

**[0015]** In an embodiment, an anti-fouling and/or foul-releasing composition is formed as a film, an aggregate, a powder, a microparticle, a nanoparticle, a core-shell particle or a combination thereof.

**[0016]** In an embodiment, an anti-fouling and/or foul-releasing composition disclosed herein is a component of a product, such as a paint, or a stand-alone coating. For example, a stand-alone coating may be affixed to a substrate by an adhesive intermediary, which in some embodiments, may be formed as a layer on the stand-alone coating and protected until use by a releasable liner. In other embodiments, an adhesive may be applied to the substrate and the stand-alone coating applied to the adhesive in a subsequent step.

**[0017]** In an embodiment, an anti-fouling and/or foul-releasing composition comprises an additive selected from the group consisting of surfactants, wetting agents, opacifiers, waxes, slip agents, drying rate modifiers, surface tension modifiers, matting agents, leveling agents, UV stabilizers, pigments and combinations thereof. The additive may be present in the coating in an amount between 0.01 - 5 wt.%, or between 0.05 - 4.5 wt.%, or between 0.1 - 4 wt.%, or between 0.2 - 3.5 wt.%, or between 0.5 - 3 wt.%, or between 0.75 - 2.5 wt.%.

**[0018]** In an embodiment, an anti-fouling and/or foul-releasing composition disclosed herein can be used on or in a product, such as a product exposed to fresh or salt water, such as but not limited to a ship hull, a buoy, a pier, a dam, a levy, a bumper, a ladder, a diving board, or a floating dock.

**[0019]** In an aspect, a method of using an anti-fouling and/or foul-releasing composition comprises applying an anti-fouling composition disclosed herein to at

least a portion of a substrate and exposing the portion of the substrate to a fresh or salt water environment. A fresh water environment may, for example, be a fresh water body of water or an air conditioning, agricultural, or food processing water system, where the anti-fouling and/or foul-releasing composition would reduce or prevent contamination from legionella, listeria, E. coli and the like.

**[0020]** In an embodiment, a substrate comprises a material selected from the group consisting of metal, plastic, fiberglass, rubber, ceramic, wood, flora, fauna and combinations thereof.

**[0021]** In an embodiment, a method of using an anti-fouling and/or foul-releasing composition comprises mixing the anti-fouling composition with an adhesive prior to applying the anti-fouling composition to a substrate. For example, the adhesive may be a resin in an amount between 1-50 wt.%, or between 1-40 wt.%, or between 1-30 wt.%, or between 2-25 wt.%, or between 4-20 wt.%, or between 5-15 wt.%. For example, the resin may be selected from the group consisting of polyvinyl butyral, polyvinyl acetate, vinyl chloride-vinyl-acetate copolymer, acrylic resin, styrene resin, polyester resin, polyurethane resin, epoxy, nitrocellulose, phenols, isocyanates, silicones and combinations thereof.

**[0022]** In an embodiment, the step of applying comprises forming the anti-fouling composition as a film on the substrate. In an embodiment, the step of applying comprises painting, spraying or drop coating a formulation comprising the anti-fouling composition onto the substrate.

**[0023]** In an aspect, a method of making an anti-fouling and/or foul-releasing composition comprises dispersing a polyhydroxyaromatic monomer, a crosslinking agent, and a biopolymer in a solvent. For example, the solvent may be selected from the group consisting of water, methanol, ethanol, n-propanol, isopropanol, butanol, octanols, acetonitrile, diacetone alcohol, benzyl alcohol, methoxy propanol, butyl glycol, glycol ethers including but not limited to ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monobutyl ether, ethylene glycol monophenyl ether, dipropylene glycol monomethyl ether, propylene glycol monoethyl ether, propylene glycol monobutyl ether, and propylene glycol monophenyl ether, methoxy butanol, ethylene glycol, propylene glycol, dioxane,

tetrahydrofuran, methyl cellulose, ethyl cellulose, butyl cellulose, methoxy propyl acetate, methyl acetate, ethyl acetate, propyl acetate, butyl acetate, 3-methoxybutyl acetate, butyl glycollate, butyl butoxyacetate, dibutyl 2,2'-oxybisacetate, dibasic esters, ethyl lactate, acetone, methylethylketone, methylisobutylketone, cyclohexanone, terpineol, acetic acid, dimethyl sulfoxide and combinations thereof.

**[0024]** In an embodiment, the solvent has a pH between 3.5 and 11.5, or between 5 and 11, or between 6 and 10.5, or between 7 and 10.5, or between 8 and 10.5, or between 9 and 10.5, or between 9.5 and 10.5.

**[0025]** In an embodiment, a method of making an anti-fouling and/or foul-releasing composition further comprises dispersing a structural material in the solvent.

**[0026]** In an embodiment, the polyhydroxyaromatic monomer, the crosslinking agent, and the biopolymer are added to the solvent sequentially or simultaneously.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0027]** Illustrative embodiments of the present invention are described in detail below with reference to the attached drawings, wherein:

**[0028]** FIG. 1 illustrates exemplary results from a paper chromatography assay showing metal binding by an anti-fouling composition disclosed herein; and

**[0029]** FIG. 2 illustrates the dimensions and spatial arrangement of test squares on a mild steel coupon used to test anti-fouling and/or foul-releasing compositions disclosed herein.

#### DETAILED DESCRIPTION

**[0030]** In general, the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The following definitions are provided to clarify their specific use in the context of this description.

**[0031]** Generally speaking, "antifouling" character is attributed to chemical or biochemical mechanisms, whereas "foul release" is attributed to physical

mechanisms. For example, antifouling may involve adaptation of the attachment surface such that it deters organism binding, dilution of quorum-sensing molecules, direct biocidal/bacteriocidal activity, induction of cell lysis, or other chemical or biochemical mechanisms. Foul release may, for example, involve weakening the attachment interface (i.e., reducing adhesive strength (force per unit area)), for example, by formation of 8-hydroxyguanine followed by the loss of Watson-Crick base pair (Guanine/Cytosine) and/or gain of Hoogsteen base pair (8-Hydroxyguanine/Adenine) resulting in the alteration of dsDNA intrastrand structure and weakening of adhesion energy or other cleavage mechanisms.

**[0032]** As used herein, "matrix" refers to a component that forms the largest fraction, at least by volume, of a mixture and that at least partially encapsulates one or more other components of the mixture.

**[0033]** As used herein, "encapsulated" refers to the position of one component or structure such that it is at least partially surrounded by one or more other components or structures.

**[0034]** As used herein, "bind", "bond" and "bound" refer to the physical attachment of one object to another or to the retention of one object by another. In an embodiment, an object can bind to / bond to or be bound to another object by an attractive force between the objects. For example, chemical species that are "bound to" one another may be covalently, ionically, or electrostatically coupled.

**[0035]** As used herein, a "crosslinker" is a molecule that chemically reacts with and covalently joins oligomers and/or polymers.

**[0036]** As used herein, a "moiety" is a part of a molecule.

**[0037]** As used herein, a "composite" comprises multiple parts or substances joined in a heterogenous configuration. Composites disclosed herein comprise a polyhydroxyaromatic polymer and at least one other material. For example, the polyhydroxyaromatic polymer may be layered with the other material, used to interpenetrate and/or encapsulate the other material, encapsulated by the other material, or otherwise intermingled with the other material.

**[0038]** As used herein, a “surfactant” is an inactive substance that imparts compositions with enhanced solubility and/or wetability.

**[0039]** As used herein, a “wetting agent” is a compound that reduces the surface tension of a liquid to allow it to spread onto a surface.

**[0040]** As used herein, an “opacifier” is a compound that blocks or reduces transmission of electromagnetic energy through a chemical mixture.

**[0041]** As used herein, “waxes” are solid to semi solid materials added to a mixture to alter surface properties like water repulsion, appearance (gloss, matting, texturing), rheology, and pigment settling.

**[0042]** As used herein, a “slip agent” is a compound acting as an internal lubricant that migrates to the surface of a mixture to reduce friction and improve slip. Surfaces with high slip characteristics are generally resistant to scratching, soiling, and blocking.

**[0043]** As used herein, a “drying rate modifier” is a compound that alters the time required to reach a tack-free drying point.

**[0044]** As used herein, a “matting agent” is a compound that changes the surface structure of a coating to scatter incident light and create a matte finish.

**[0045]** As used herein, a “leveling agent” is a compound that improves flow of a liquid product, thereby allowing the product to fill any irregularities that may be present on a surface.

**[0046]** As used herein, a “UV stabilizer” is a compound that combats degradation of polymers exposed to light, oxygen and/or heat and extends the life of a finished product by protecting against loss of strength, stiffness, flexibility and gloss.

**[0047]** The terms “direct and indirect” describe the actions or physical positions of one object relative to another object. For example, an object that “directly” acts upon or touches another object does so without intervention from an intermediary. Contrarily, an object that “indirectly” acts upon or touches another object does so through an intermediary (e.g., a third component).

**[0048]** Briefly, the compositions disclosed herein are designed to perform as potent antifouling materials by employing three antifouling/foul release mechanisms, which are described in connection with exemplary materials below, without intending to limit the disclosed compositions or to be bound by theory.

**[0049]** *First mechanism (Redox Antifouling Mechanism):* Positively-charged polycatechol polymers are crosslinked with, for example dithiols, via a novel synthetic procedure which maximizes free amino groups on the polymeric aggregate. These free amines are reactive and easily functionalized under mild conditions. The antimicrobial properties of polycationic species have long been recognized and are generally non-toxic to multicellular eukaryotes. Since these polymers are covalently linked to the other components of the anti-fouling compositions, and because of their large sizes and high molecular weights, they are rendered non-leachable and any dispersion via wear or erosion yields insoluble particulate material. Furthermore, the affinity of polycatechols for multivalent heavy-metal ions leads to locally high concentrations of cations (e.g., copper, lead, and iron) at the solid-liquid interface. Polycatechols are also known to reduce heavy-metal ions (such as  $\text{Ag}^+$ ) to their elemental form, which possesses anti-microbial properties. After sloughing from the anti-fouling composition, or a marine paint or coating containing the anti-fouling composition, as a result of inevitable wear, such particles are destined for benthic ocean domains that are a well-known environmentally innocuous sink for such metals. For years, harbors, ports, and waterways have been contaminated with copper ions from marine antifouling paints, often at dangerously high concentrations. This component of the anti-fouling composition therefore performs an environmentally friendly bioremediation function while simultaneously leveraging existing pollutants as antifouling agents. Additionally, the polyradical nature and inherent redox activity of polycatechols, in combination with the cysteine moieties introduced via the dithiol groups, serve to interfere directly with the critical first substrate attachment mechanism of various macrofouling species, including barnacles.

**[0050]** Due to the intriguing nature of polycatechol polymerization chemistry, films, aggregates and/or nanoparticles may be synthesized in the presence of proteins, nucleic acids, small molecules, or other polymeric oligomers. When

performed in this manner, such species are entrapped within the polycatechol polymer or matrix. Certain acidic proteins added during catechol polymerization are able to promote solution-based, rather than surface-associated, polymerization. These proteins recruit catechol monomers and higher-order oligomers during the polymerization process and yield small-diameter (c. 100 nm) nanoparticles with low polydispersity indices. Alternatively, catechol may polymerize within and around proteins and other biopolymers/composite materials that are either adsorbed to various substrates as thin films, or throughout and around insoluble particulate matter dispersed in the reaction mixture. By controlling the aqueous reaction conditions such as pH, ionic strength, and buffer composition, monomers may diffuse through porous materials or hydrogel networks prior to the initiation of polycatechol formation. These intriguing properties allow for a wide range of temporally dependent synthetic processes that can yield diverse libraries of anti-fouling compositions with tunable charge-densities, elastic moduli, physicochemical surface properties, and domain sizes.

**[0051]**     *Second mechanism (Cleavage Antifouling Mechanism):* Salmon-derived double stranded DNA (dsDNA) can be incorporated into the anti-fouling composition with the polycatecholic polymer. The negatively charged phosphate backbone of the DNA helix is strongly attracted to polycationic materials, often undergoing collapse or condensation as a result of charge-pairing interactions. Due to its ability to intercalate planar polycyclic molecules and complex polyvalent heavy-metal ions, dsDNA in the anti-fouling composition also has the potential to attract other environmental pollutants such as polycyclic aromatic hydrocarbons (PAH) and reactive dyes such as Methylene Blue. Concentration of such species at the solid-liquid interface serves to further heighten the anti-fouling composition's generation of an inhospitable environment for attachment and growth of both micro- and macrofoulers. Moreover, to the extent that bacterial invaders attempt to make the phenotypic switch from a planktonic lifestyle to a potentially biofilm-inducing adsorbate, their export of DNA hydrolytic enzymes has been shown to increase by up to two orders of magnitude during their secretion of extracellular matrix components. As the DNA of the anti-fouling composition is cleaved, the local cross-linking density of the anti-fouling composition is reduced, which has a three-pronged effect. First, the water content increases as crosslinks are severed, yielding

hydrostatic pressure changes that are, in and of themselves, potentially harmful to any nascent bacterial biofilm microcolonies. Secondly, neighboring polymeric chains recede from one another as water content increases, concomitantly increasing the distance between adjacent bacterial cells, interfering with cell-to-cell contacts, and diluting the concentration of quorum-sensing molecules (such as acyl homoserine lactones for Gram-negative bacteria). Third, if enough dsDNA chains are cleaved via bacterially derived DNase enzymes, the local bacteria embedded in the matrix will detach from the anti-fouling composition (e.g., paint or coating) into the surrounding aquatic milieu. This allows for the anti-fouling composition to act as a "foul-release" coating. As the bacterial cells undergo such stressors, many will undergo cellular lysis or autolysis, releasing bacterial DNA and reactive-oxygen species (ROS) into the microenvironment. Under such conditions, one can expect that inter- and intra-strand covalent DNA-crosslinking will take place. This serves to replenish the anti-fouling composition's DNA lost during the foul-release process, regenerating the DNA functionality of the material.

**[0052]** Broad band energy dissipation of polycatechol

**[0053]** Aspects of the molecular features that permit the physical assembly of polydopamine/polycatechol domains, namely the extended conjugated  $\pi$  electron system and cationic moieties, also provide the route for the broad band electromagnetic energy absorption and dissipation exhibited by these types of systems.

**[0054]** The heterogeneous domain polydispersity and composition result in a broad distribution of the sizes of the conjugated  $\pi$  electron systems available to interact with electromagnetic radiation. These  $\pi$  domains are the "antennae" that receive the electromagnetic radiation that their size has them "tuned to". The distribution in sizes leads to the distribution in wavelengths absorbed. The photons at various wavelengths present in the solar emission in the troposphere are efficiently absorbed by the highly coupled electronic system. The broad banded nature of the absorbing domains and the high degree of coupling efficiently distributes the photons' energy across the electronic network. Intersystem crossing permitted by quantum mechanics governing the behavior of the  $\pi$  electron system can then transfer the excited state electronic energy into the rotational-vibrational

manifold. From there the molecular rotations and vibrations, also governed at the level of quantum mechanics, can dissipate the energy into the environment as thermal energy.

**[0055]** This distribution and subsequent conversion of the photonic energy into thermal energy serves to protect the molecular bonds and provide a durability to the structure. The polydopamine structures are similar to melanin and often used as models for this biologically relevant compound. A function of melanin in nature is to provide protection from UV light damage in such systems as mammalian skin through mechanisms analogous to those described above.

**[0056]** Recent studies of melanin have indicated that it can function as a photosensitizer when energy transference occurs. (Solano) Thus UV stabilizing additives may be used in some formulations of polydopamine/polycatechol materials. Melanin has been used as a photosensitizer in hydrogel systems (Ninh et al.).

**[0057]** Hong *et al.*, Progressive fuzzy cation- $\pi$  assembly of biological catecholamines. *Sci. Adv.* 2018: 4(9), 7 September 2018.

**[0058]** C. Ninh *et al.*, Photoresponsive hydrogel networks using melanin nanoparticle photothermal sensitizers. *Biomater. Sci.*, 2014, 2(5), 766-774. 1 April 2014.

**[0059]** F. Solano, Photoprotection versus photodamage: updating an old but still unsolved controversy about melanin. *Polymer International*, 65(11), Nov. 2016, pages 1276-1287. First published: 08 April 2016.

**[0060]** *Third mechanism (ROS (Reactive Oxygen Species) Antifouling Mechanism):* DNA is known to form adducts with various proteins upon irradiation, plasma-treatment, and ROS-generating processes such as the Fenton Reaction, frequently generating multiple points of attachment among the protein and multiple DNA molecules that provide a desirable dendromeric aspect to the anti-fouling composition. Albumins (such as Bovine Serum Albumin) are ubiquitous proteins that exhibit multiple functional aspects including fatty acid-binding and chemical catalysis. Intriguingly, albumin-bound  $\text{Fe}^{2+}$  and  $\text{Cu}^+$  ions have been shown to react with hydrogen peroxide (a bacterially derived ROS) to yield the highly reactive but short-

lived (and thus active only in the immediate microenvironment) hydroxyl radical. In addition to its bacteriocidal properties, hydroxyl radical is known to form lesions on dsDNA that may lead to depurination reactions and inter/intrastrand crosslinking, which serve to further reinforce the integrity and functionality of the anti-fouling composition.

**[0061]** Finally, inclusion of inorganic nanoparticles, such as silica or titania, allows for anchoring of multiple anti-fouling composition functional groups that may further reinforce the physical properties of the material. Intriguingly, anatase titania reacts with dissolved molecular oxygen to yield superoxide radicals and singlet oxygen that are inherently reactive and bacteriocidal and also provoke hydroxyl radical release from hydrogen peroxide. Again, such ROS serve to reinforce cross-linking density in the anti-fouling composition.

**[0062]**  $\text{TiO}_2$  superoxide radicals

**[0063]** Titanium Oxide ( $\text{TiO}_2$ ) of particular morphology is known to exhibit photocatalyst activity (PCA) capable of producing Reactive Oxygen Species (ROS) generated by reduction and oxidation of water or oxygen. One such ROS is superoxide. The PCA of  $\text{TiO}_2$  is most often associated with the anatase morphology. Typically the generation of ROS on  $\text{TiO}_2$  requires activation with UV light. Nanoparticles of  $\text{TiO}_2$  have been utilized for this purpose because the morphology of the nanocrystals can be controlled to a great extent. The increased surface area is a consequence of the smaller scale(s) of the nanocrystals. Crystal thicknesses less than 15nm have exhibited higher PCA than polycrystals.

**[0064]** PCA enhancement has been reported with mixtures of  $\text{TiO}_2$  powders and activated carbon, graphene, and carbon nanotubes. The enhancement has been attributed to the carbon forms acting as a photosensitizer absorbing more light with extension into the visible wavelengths. Also the carbon promotes surface reactions at the active sites through its well known property of providing higher absorption of organic compounds.

**[0065]** Co-formation of anatase and rutile domains in intimate proximity in the presence of carbon has been demonstrated to provide a high degree of PCA and

extend the excitation wavelengths into the visible. Any of these approaches could be used to provide additive TiO<sub>2</sub> to boost the ROS mechanism of antifouling.

**[0066]** S.P. Krumdieck *et al.* Nanostructured TiO<sub>2</sub> anatase/rutile-carbon solid coating with visible light antimicrobial activity. Scientific Reports, (2019) 9:1883.

**[0067]** Yang Mi and Yuxiang Weng. Band Alignment and Controllable Electron Migration between Rutile and Anatase TiO<sub>2</sub>. Scientific Reports. (2015) 5:11482.

**[0068]** TiO<sub>2</sub> heat dissipation

**[0069]** Colloidal suspensions of nanoparticles in the size range of 1–100 nm in base fluids are known as nanofluids. TiO<sub>2</sub> nanoparticles have been studied as nanofluids. (Hafiz Muhammad Ali and Waqas Arshad, Thermal performance investigation of staggered and inline pin fin heat sinks using water based rutile and anatase TiO<sub>2</sub> nanofluids. Energy Conservation and Management, vol. 106, pages 793-803, December 2015.) Rutile and anatase forms of TiO<sub>2</sub> have been shown to improve heat transfer in aqueous based TiO<sub>2</sub> nanofluids using two heat exchanger geometries, in-line, and staggered pin fin heat sinks. The rutile form increases the heat transfer efficiency to a greater extent than the anatase form.

**[0070]** The Nusselt number is the ratio of convective to conductive heat transfer across a boundary and can indicate an improvement in heat transfer. The enhanced relative heat transfer of the TiO<sub>2</sub> nanofluids is demonstrated by comparing the Nusselt number measure for the two nanofluids in the two geometries relative to the Nusselt number for distilled water.

**[0071]** These results point to a parameter to choose for insulative or dissipative coatings in terms of heat based on the choice of TiO<sub>2</sub> morphology for this additive.

**[0072]** The compositions and methods disclosed herein are further illustrated by the following Examples. These Examples are for illustrative purposes only and are not intended to limit the invention.

## EXAMPLE 1

**[0073]** This Example illustrates the general experimental protocol for synthesizing an anti-fouling composition disclosed herein. The steps described may be performed in any sequence.

**[0074]** Where zeolite is used any water-insoluble particulate may be substituted for the zeolite. Any alkaline material (at any concentration and at any pH) may substitute for potassium carbonate (0.1 M, pH = 8.5). Any proteinaceous or peptide-like compound may substitute for Bovine Serum Albumin. Any nucleic acid may substitute for Salmon Sperm dsDNA (e.g., prokaryotic/Archaea or eukaryotic dsDNA, any such single-stranded DNA resulting from heat or chaotropic denaturation or analogous RNA, any viral dsDNA, ssDNA, or RNA, or any circular bacterial plasmid DNA, or any exosomes or vesicular packaged and extracellularly transported nucleic acid or protein/nucleic acid-containing liposomes, micelles, microparticles or nanoparticles from prokaryotic or eukaryotic cells comprising, but not limited to, viral, prokaryotic, eukaryotic, prion, or Archaea-derived proteins and/or nucleic acids and/or polysaccharides and/or GAGs, proteoglycans, mucins, etc.). Any reducible metal ion, diatomic halide (e.g., chlorine gas or bromine liquid), reducible gas or liquid (e.g., oxygen gas or ozone, ionic liquids/deep eutectic solvents), plasma-treated/plasma-activated water or polyatomic species (e.g., ammonium persulfate) may substitute for Cu(II). Water may be degassed/charged with inert gas via, e.g., sonication, bubbling with argon, nitrogen, carbon dioxide, oxygen, ozone, helium, et al.).

**[0075]** The components may be added in any order. The concentration ranges for all components range from 0 mg/mL – 2,000 mg/mL, with the concentration (mass per unit volume) of insoluble particulate material being limited only by practical considerations.

**[0076]** Additional components may be added to the anti-fouling compositions disclosed herein. Such additional components include, but are not limited to, any proteinaceous material, peptide-like compound, protein-like nucleic acids, mono-, di-, or polysaccharides (e.g. laccases, chitosan, hyaluronuric acid, trehalose, propylene glycol), or synthetic polymers (e.g., PVA, PAA, PMAA, PMMA, Polyamides,

Polyurethanes, PEI, Dendrimeric Monomers/Polymers, Polyacrylamide, or block copolymers formed from such homopolymers, e.g. via *in situ* crosslinking prior to, during, or after polymerization). Anti-microbial peptides (AMPs, e.g., LL-37) and/or neuropeptides (e.g., Substance P, Calcitonin Gene-Related Peptide, Vasoactive Intestinal Peptide, Neuropeptide Y, etc.) and/or natural peptidyl/proteinaceous venoms/poisons (e.g. Honeybee Melittin, Pufferfish Tetrodotoxin, Poison Arrow Frog Lipophilic Alkaloid Toxins (e.g., histrionicotoxin) or any such preparations (e.g., curare, inee).

**[0077]** Typical Synthetic Protocol

- 1) Particulate Material (Bentonite) is suspended in Distilled or Nanopure Water – 3000 mg/90 mL, with magnetic stirring – in three reaction vessels that are open to the atmosphere
- 2) Water (Blank)/Catechol/Dopamine is added to stirring particulate material – 300 mg/30 mL – all at once
- 3) Reaction proceeds for 1 hour. 25 mL reserved from each vessel. Aliquots from each vessel are spotted onto filter/chromatography paper to determine coherence/fluid properties/color/etc.
- 4) 10 mL 0.1 M Potassium Carbonate (“Base”) at pH = 8.5 added to each reaction vessel
- 5) Reaction proceeds for 1 hour. 25 mL reserved from each vessel. Aliquots from each vessel are spotted onto filter/chromatography paper to determine coherence/fluid properties/color/etc.
- 6) 250 mg Bovine Serum Albumin Lyophile (solid) added to each vessel
- 7) Reaction proceeds for 1 hour. 25 mL reserved from each vessel. Aliquots from each vessel are spotted onto filter/chromatography paper to determine coherence/fluid properties/color/etc.
- 8) 100 mg ds Salmon Sperm DNA Lyophile (solid) added to each vessel
- 9) Reaction proceeds for 1 hour. 25 mL reserved from each vessel. Aliquots from each vessel are spotted onto filter/chromatography paper to determine coherence/fluid properties/color/etc.
- 10) 5 mL Copper (II) Sulfate (10 mg/mL) added to each vessel

11) Reaction proceeds for 1 hour. Remaining suspension is reserved. Aliquots from each vessel are spotted onto filter/chromatography paper to determine coherence/fluid properties/color/etc.

**[0078]** Subsequently, samples are either lyophilized to dryness and added to paint formulations, drop-cast on substrates, or dip-coated on substrates and placed into fouling aquaria, and ultimately compared to untreated substrates or substrates treated with standard anti-fouling paints.

**[0079]** Gravimetric Tests, Biological Staining, FTIR-ATR, Fluorescence, Microscopy, Immunohistochemistry, etc., are utilized for evaluating antifouling efficacy.

**[0080]** Paper Chromatographic Heavy Metal Reduction Assay

**[0081]** The well known bicinchoninic (BCA) assay for determination of protein concentration was adapted for the present anti-fouling compositions. The traditional BCA assay involves: Solution A (pH = 11.25): 1.  $K_2CO_3$  (8.0% w/v), 2.  $Na_2C_4H_4O_6$  (1.4% w/v). Solution B: Bicinchoninic acid (4.0% w/v). Solution C:  $CuSO_4$  (4.0% w/v). Solutions A/B/C are combined in a ratio of 26:25:1. Aliquots of protein solution are added to the mixture and the mixture is incubated. Bovine serum albumin (BSA) is the most commonly used protein standard. Increased reaction time and/or temperature result in increased signal intensity with no true endpoint. The reaction proceeds until  $Cu^{2+}$  is consumed.  $Cu^{2+}$  does not interact with BCA. It is chelated by tartrate ions.  $Cu^{2+}$  is reduced to  $Cu^+$  by peptide-bond nitrogens (also Cys/Trp/Tyr).  $Cu^+$  forms a stable, highly colored complex with BCA. Samples are read on a UV-Vis Spectrophotometer (562 nm).

**[0082]** The modified assay uses 2,9-dimethyl-1,4-phenanthroline (neocuproine) instead of BCA in Solution B. Neocuproine is less expensive than BCA and the neocuproine-Cu(I) complex has a higher extinction coefficient than the BCA-Cu(I) complex. Solution C contains BSA rather than  $CuSO_4$ . Aliquots of  $CuSO_4$  solution incubated with the anti-fouling compositions are added to the Solution A/B/C mixture. Cu(II) is reduced to Cu(I) by peptide-bond nitrogens (also Cys/Trp/Tyr). Incubation

time and temperature are optimized for the modified assay. Samples are read on a UV-Vis Spectrophotometer at about 460-480 nm.

**[0083]** Filter paper or chromatography paper is infused with 1. neocuproine solution, 2.  $\text{CuSO}_4$  solution, 3. neocuproine solution, then  $\text{CuSO}_4$  solution, 4. water (control). The paper is allowed to dry after each individual infusion. Anti-fouling suspensions (5-10  $\mu\text{L}$ ) are spotted on each treated paper. Reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$  yields a red-orange area either atop or encircling a copper-reduced anti-fouling composition spot. The  $\text{Cu(II)}$ /ascorbic acid redox system may be used as a positive control for the neocuproine paper (requires both ascorbic acid and  $\text{Cu(II)}$ ) or Neo- $\text{Cu(II)}$  paper (requires only ascorbic acid). Copper sulfate infused paper can indicate the degree of cohesion induced by  $\text{Cu(II)}$  relative to control (water). This becomes a more useful/powerful technique when an anti-fouling composition spot is "overspotted" with potentially damaging/disruptive compounds after fixation with  $\text{Cu(II)}$ .

**[0084]** FIG. 1 illustrates exemplary results from a paper chromatography heavy metal reduction assay (described above) showing metal binding by an anti-fouling composition disclosed herein. The assay of FIG. 1 was performed holding the anti-fouling composition concentration constant for each spot. A control with no anti-fouling composition appeared in the last lane to the right. The air dried spots were then "over-spotted" with drops of  $\text{Ag}^+$  solution of increasing concentration. The concentration of  $\text{Ag}^+$  ranged from 0 to 160 mg/ml (0 mg/ml, 5 mg/ml, 10 mg/ml, 20 mg/ml, 40 mg/ml, 80 mg/ml 160 mg/ml). The last two lanes had the maximum concentration of  $\text{Ag}^+$  (160 mg/ml).

**[0085]** The redox reaction occurring in the anti-fouling composition after over-spotting is indicated by the darkening of the original spot over the course of several minutes following over-spotting. Chromatography indicates a range of aggregation/polymerization in the anti-fouling composition following exposure to the  $\text{Ag}^+$ . The anti-fouling composition that saw no silver exhibited a high mobility in the aqueous mobile phase. Upon developing, the degree of sequestration of  $\text{Ag}^+$  is seen to have varied across the ranges of  $\text{Ag}^+$  concentration.

**[0086]** In some embodiments, instead of paper, cylindrical tubes packed with chromatographic material can be run in one direction with, for instance, water as the mobile phase to separate metal ions from organic/inorganic materials. In a second step, the cylindrical tube is inverted and dried, e.g., by forced air, followed by utilization of a mobile phase containing reductants specific to the metal ion of choice. After the two runs, the reduced metal ions of interest (often colored and with large extinction coefficients) would lie behind an optical window and the tube is placed into a standard cuvette and run on a standard UV-Vis Spectrophotometer.

#### EXAMPLE 2

**[0087]** Abrasion and wear models on polymeric, metal, and glass surfaces have shown that coatings of the anti-fouling and/or foul-releasing compositions are robustly attached to the substrates. Water contact angle-testing clearly indicates large changes in surface energy upon attachment of the compositions.

#### EXAMPLE 3

**[0088]** This Example illustrates heavy metal reduction by the compositions disclosed herein.

**[0089]** A gel of Polyvinyl Alcohol and Boric Acid was generated (4.0%:0.4% w/w in NanoPure Water), in addition to the same gel with the addition of either Salmon Sperm dsDNA, Bovine Serum Albumin (BSA) or both:

- A) PVA/Borate only
- B) Salmon Sperm dsDNA (1 mL @ 100 mg/mL)
- C) Bovine Serum Albumin (1 mL @ 100 mg/mL)
- D) Salmon Sperm dsDNA + Bovine Serum Albumin (both 1 mL @ 100 mg/mL)

**[0090]** Post gelation, the samples were frozen at -80 °C overnight and then placed on a lyophilizer until the entirety of the frozen water had sublimed from the samples.

**[0091]** Subsequently, each 40 mg of each lyophile was added to 4 10 mL Borosilicate Glass Culture Tubes and treated differentially in the following manner:

1. Lyophile + 1 mL NanoPure Water
2. Lyophile + 1 mL Dopamine Hydrochloride (20 mg/mL) + 1 mL NanoPure Water
3. Lyophile + 1 mL Dopamine Hydrochloride (20 mg/mL) + 1 mL Silver Nitrate (@ 10 mg/mL)
4. Lyophile + Solid Dopamine Hydrochloride (20 mg) + 1 mL Silver Nitrate (@ 10 mg/mL)

**[0092]** Subsequently, nine further aliquots were added to each tube (A1-D4 through A4-D4) based upon the nature of the particular experiment (controls vs. experimental treatments). So, for A1/B1/C1/D1, 1 mL of Silver Nitrate was added to each over the course of five days (one addition at 10:00 A.M. and one addition at 10:00 PM); for A2/B2/C2/D2, 1 mL NanoPure Water was added at the same frequency as the above; for A3/B3/C3/D3, 1 mL Silver Nitrate (@ 10 mg/mL); for A4/B4/C4/D4, 1 mL Silver Nitrate (@ 10 mg/mL).

**[0093]** For A4 and B4, elemental silver metal was evident after the passage of several days. This was shown by the lack of birefringent color polymorphism for pure reduced Ag(s) crystals. Thus, the ability of the formulations to reduce silver (I) ion to silver metal was indicated.

**[0094]** To confirm the existence of the above, all of the material in the test tube was subjected to the following chemical tests/experiments in sequence:

- 1) Addition of an equal volume of Ammonium Hydroxide solution (3 M) to complex unreduced silver (I) ion. Aqueous layer was removed and reserved from solid product
- 2) Addition of 3 mL of concentrated HCl to remove/dissolve any silver (I) ions contained within organic complexes. Aqueous layer was removed and reserved from solid product

- 3) Addition of concentrated Nitric Acid (3 mL) which is able to oxidize and dissolve reduced silver metal
- 4) The pH of the Nitric/Silver solution was adjusted to 8.0 via the addition of solid Sodium Bicarbonate. Copper wire was then placed into the neutralized solution and the wire was monitored for the deposition of reduced silver metal after overnight incubation

**[0095]** Silver deposition on the copper wire is indicative of the ORIGINAL presence of reduced silver metal in the various formulations, since all unreacted silver (I) ion is removed in Steps 1-2 and any silver (I) present after the addition of concentrated nitric acid can only have been sourced from reduced silver metal.

**[0096]** Silver deposition on the copper wire was clearly evident the following morning, subsequent to the incubation of copper wire in the neutralized concentrated nitric acid fraction and is direct evidence for the reduction of silver (I) ion by the compositions disclosed herein.

**[0097]** The identification of the reduced silver ion by lack of polymorphic birefringence followed by the observation of the growth of reduced silver metal on the copper wire after treatment with ammonia, HCl, and Nitric Acid provides unequivocal evidence for the capacity of the polyradical materials disclosed herein to reduce silver (I) ion to silver metal.

**[0098]** In a separate but similar experiment, the above scenario was repeated with Copper (II) Sulfate Ion in lieu of Silver (I) Nitrate. Reduction of Copper (II) ion to Copper (I) ion was monitored by the inclusion of the Copper (I) ion chelator Neocuproin, which turns a bright orange color in the presence of Copper (I) ion in aqueous solution.

**[0099]** The Control for the above with the aforementioned materials is a solution of Copper (II) Sulfate with Ascorbic Acid, known to reduce Copper (II) ion to Copper (I) ion.

**[00100]** The elution of the added Copper (II) Sulfate Ion from materials A-D above into a tube with a solution of Neocuproine revealed the presence of Copper (I) ions in materials A and B.

**[00101]** Since the Reduction Potentials vs. SCE for the above are both known, it is evident that, at least, any metal ion which falls within the range of those reduction potentials must also be reducible by the materials listed above, but these experiments do not preclude the reduction of any other metal ion species which falls outside of the Cu(II) – Ag(I) range.

#### EXAMPLE 4

**[00102]** This Example illustrates foul-release via biological agents for coatings of the compositions disclosed herein.

**[00103]** A material composed of Titanium (II) Oxide and Salmon Sperm dsDNA was synthesized via sequential addition of Anatase Titania and Salmon Sperm dsDNA (1.1 grams total @ 1 gram Titania:100 mg dsDNA) to 100 mL NanoPure Water.

**[00104]** The reaction mixture was placed into fritted columns (0.2 micron) and the water was eluted under positive gas pressure until only solid material remained on the frits of the columns. The output of the columns were blocked by the insertion of the appropriate threaded screw.

**[00105]** Subsequently, Methylene Blue (MB) was added (10 mL @ 100 mg/mL) to the solid material in the column and the solid material was resuspended in the Methylene Blue solution.

**[00106]** In order to demonstrate the activity of biological nucleases in the aquariums or the Intracoastal Waterway, it was necessary to covalently link the MB (which intercalates between adjacent DNA base pairs) to the DNA molecule via generation of an adduct. Addition of Copper (II) Sulfate and Ascorbic Acid (both at 10 mg/mL at 10% v/v ratios) under the influence of UV-A/UV-B/UV-C light in the presence of anatase Titania has been shown to catalyze the formation of MB/dsDNA adduct. The light was administered to the various samples for 4 hours.

**[00107]** The permutations of the four samples were as follows:

**[00108]** A) Anatase Titania/dsDNA followed by the addition of Copper (II) Sulfate followed by Ascorbic Acid

**[00109]** B) Anatase Titania/dsDNA followed by the addition of Ascorbic Acid followed by the addition of Copper (II) Sulfate

**[00110]** C) dsDNA ONLY followed by the addition of Copper (II) Sulfate followed by Ascorbic Acid

**[00111]** D) dsDNA ONLY followed by the addition of Ascorbic Acid followed by Copper (II) Sulfate

**[00112]** The formation of the adduct under the above conditions is necessary to prove catalytic activity of natural aquarium water or seawater DNase enzymes or similar enzymes dedicated to nucleic acid remodeling during the formation of, for example, bacterial biofilms. If the dsDNA/MB association is NOT covalent in nature, then any experimental result could simply be the result of ionic strength or pH effects, as regards the measured leaching of MB from the solid DNA or Titania/DNA samples. Since the association between MB and dsDNA has covalent nature, release of MB from the materials above the column frit MUST be the result of actual cleavage of the DNA chain (including those stretches of DNA sequence which contain covalently-bound MB-DNA adducts).

**[00113]** All four of the above dsDNA/MB containing adducts were rinsed 5 times with 10 ml NanoPure water to remove/elute any unreacted MB dye. After the elutions ran colorless, the materials in A-D were dried in a vacuum oven (30 degrees Celsius for 10 days), removed from the columns, weighed and then split into TWO new columns. Thus each of the four initial materials has been rinsed of unreacted MB dye, dried, and then split equally into two new columns (A1/A2, B1/B2, C1/C2, D1/D2, etc.)

**[00114]** Fouling aquariums were configured as 10-gallon saltwater systems seeded with organisms from the Florida Intracoastal Waterway and supplemented with phytoplankton. The tanks were maintained with alternating white light, UV001

light, and dark cycles on a daily basis, and kept under constant aeration at 30 degrees Celsius.

**[00115]** Water was removed from the main fouling aquarium into 50 mL Falcon Tubes, capped, and heated to 95 degrees Celsius in a water bath for four hours. Caps were NOT removed until use.

**[00116]** Each of the 8 Columns (2 each for A/B/C/D) were then eluted with 20 mL of the “boiled” aquarium water and left overnight at room temperature. All liquid was eluted and reserved.

**[00117]** The columns containing A1/B1/C1/D1 materials were eluted AGAIN with Boiled Aquarium water whereas A2/B2/C2/D2 materials were eluted with UNBOILED Aquarium Water, with the presumption that any bacteria or DNase enzymes in the UNBOILED samples would retain their biological activity to the extent that enzymatic cleavage of the DNA/MB adducts would still be evident IF such species did (as predicted) exist in natural waters.

**[00118]** The color profiles (from the MB) in the BOILED vs. UNBOILED experiments were compared as appropriate (i.e., A1 vs. A2, B1 vs. B2, etc.) and the optical densities of the eluent of the samples treated with the UNBOILED aquarium water were, in all cases, at least 4-fold greater than that of the BOILED aquarium water samples, indicating the presence of catalytically/enzymatically active species, as previously hypothesized.

**[00119]** To support the above observations, after complete elution of any liquids from the A1-D1 samples, the materials were again dried under vacuum at 30 degrees C for 10 days, and the masses of the remaining materials were compared. According to the hypothesis, any materials subjected to viable bacterial species or soluble DNase enzymes would evince a LOWER MASS than those which were subjected to BOILED (i.e., without viable bacteria or DNase enzymatic activity), since in the latter (boiled) case DNA was uncleaved and could not pass through the column frit.

**[00120]** Indeed, the masses observed were proportional to the ratios of MB optical activity (i.e., blue color) seen in the experiment outlined above, once the contribution

of anatase Titania to the overall mass was corrected such that only the DNA component was considered.

**[00121]** Overall, the results clearly indicate that the fouling of the materials disclosed herein by bacterial species can lead to the cleavage of the dsDNA in the formulation and thus the release of the fouling bacteria from treated surfaces as a result of their own catalytic activities.

#### EXAMPLE 5

**[00122]** This Example evaluates field deployed anti-fouling efficacy of compositions disclosed herein as paint additives.

**[00123]** Materials were synthesized as described previously. The library of synthesized materials is presented in Table 1. The order of addition of the various modular anti-fouling components may be modified while maintaining the timing of each addition within any permutation, as well as the ratios of masses added for the various modules for any permutation.

Table 1

| Sample ID# | Particulate | Active   | Base | BSA | DNA | Cu(II) | Total Mass (mg) |
|------------|-------------|----------|------|-----|-----|--------|-----------------|
| 1          | Bentonite   | Dopamine |      |     |     |        | 515.8           |
| 2          | Bentonite   | Dopamine | Base |     |     |        | 515.7           |
| 3          | Bentonite   | Dopamine | Base | BSA |     |        | 678.1           |
| 4          | Bentonite   | Dopamine | Base | BSA | DNA |        | 582.6           |
| 5          | Bentonite   | Dopamine | Base | BSA | DNA | Cu(II) | 772.8           |
| 6          | Bentonite   | Catechol |      |     |     |        | 263.8           |
| 7          | Bentonite   | Catechol | Base |     |     |        | 531.4           |
| 8          | Bentonite   | Catechol | Base | BSA |     |        | 627.0           |
| 9          | Bentonite   | Catechol | Base | BSA | DNA |        | 608.8           |
| 10         | Bentonite   | Catechol | Base | BSA | DNA | Cu(II) | 1185.7          |
| 11         | Bentonite   | Water    |      |     |     |        | 230.2           |
| 12         | Bentonite   | Water    | Base |     |     |        | 397.4           |
| 13         | Bentonite   | Water    | Base | BSA |     |        | 509.1           |
| 14         | Bentonite   | Water    | Base | BSA | DNA |        | 617.0           |
| 15         | Bentonite   | Water    | Base | BSA | DNA | Cu(II) | 972.0           |
| 16         | Lignin      | Dopamine |      |     |     |        | 481.7           |
| 17         | Lignin      | Dopamine | Base |     |     |        | 400.2           |
| 18         | Lignin      | Dopamine | Base | BSA |     |        | 580.5           |

|    |         |          |                              |     |     |        |        |
|----|---------|----------|------------------------------|-----|-----|--------|--------|
| 19 | Lignin  | Dopamine | Base                         | BSA | DNA |        | 473.4  |
| 20 | Lignin  | Dopamine | Base                         | BSA | DNA | Cu(II) | 762.8  |
| 21 | Lignin  | Catechol |                              |     |     |        | 612.6  |
| 22 | Lignin  | Catechol | Base                         |     |     |        | 594.0  |
| 23 | Lignin  | Catechol | Base                         | BSA |     |        | 393.3  |
| 24 | Lignin  | Catechol | Base                         | BSA | DNA |        | 551.9  |
| 25 | Lignin  | Catechol | Base                         | BSA | DNA | Cu(II) | 1101.3 |
| 26 | Lignin  | Water    |                              |     |     |        | 397.6  |
| 27 | Lignin  | Water    | Base                         |     |     |        | 531.7  |
| 28 | Lignin  | Water    | Base                         | BSA |     |        | 503.6  |
| 29 | Lignin  | Water    | Base                         | BSA | DNA |        | 467.2  |
| 30 | Lignin  | Water    | Base                         | BSA | DNA | Cu(II) | 607.3  |
| 31 | Titania | Dopamine |                              |     |     |        | 258.3  |
| 32 | Titania | Dopamine | Base                         |     |     |        | 215.8  |
| 33 | Titania | Dopamine | Base                         | BSA |     |        | 684.9  |
| 34 | Titania | Dopamine | Base                         | BSA | DNA |        | 637.7  |
| 35 | Titania | Dopamine | Base                         | BSA | DNA | Cu(II) | 541.5  |
| 36 | Titania | Catechol |                              |     |     |        | 556.2  |
| 37 | Titania | Catechol | Base                         |     |     |        | 589.0  |
| 38 | Titania | Catechol | Base                         | BSA |     |        | 714.6  |
| 39 | Titania | Catechol | Base                         | BSA | DNA |        | 717.6  |
| 40 | Titania | Catechol | Base                         | BSA | DNA | Cu(II) | 794.9  |
| 41 | Titania | Water    |                              |     |     |        | 255.5  |
| 42 | Titania | Water    | Base                         |     |     |        | 534.0  |
| 43 | Titania | Water    | Base                         | BSA |     |        | 654.2  |
| 44 | Titania | Water    | Base                         | BSA | DNA |        | 609.8  |
| 45 | Titania | Water    | Base                         | BSA | DNA | Cu(II) | 1006.9 |
| 46 | Zeolite | Dopamine |                              |     |     |        | 455.9  |
| 47 | Zeolite | Dopamine | Base                         |     |     |        | 650.4  |
| 48 | Zeolite | Dopamine | Base                         | BSA |     |        | 649.3  |
| 49 | Zeolite | Dopamine | Base                         | BSA | DNA |        | 479.2  |
| 50 | Zeolite | Dopamine | Base                         | BSA | DNA | Cu(II) | 1221.0 |
| 51 | Zeolite | Catechol |                              |     |     |        | 516.0  |
| 52 | Zeolite | Catechol | Base                         |     |     |        | 643.3  |
| 53 | Zeolite | Catechol | Base                         | BSA |     |        | 604.5  |
| 54 | Zeolite | Catechol | Base                         | BSA | DNA |        | 579.4  |
| 55 | Zeolite | Catechol | Base                         | BSA | DNA | Cu(II) | 1206.9 |
| 56 | Zeolite | Water    |                              |     |     |        | 396.0  |
| 57 | Zeolite | Water    | Base                         |     |     |        | 444.8  |
| 58 | Zeolite | Water    | Base                         | BSA |     |        | 594.1  |
| 59 | Zeolite | Water    | Base                         | BSA | DNA |        | 683.8  |
| 60 | Zeolite | Water    | Base                         | BSA | DNA | Cu(II) | 954.1  |
| 61 | Titania | Dopamine |                              |     |     |        | 1144.0 |
| 62 | Titania | Dopamine | Base                         |     |     |        | 3137.3 |
| 63 | Titania | Dopamine | Base<br>(Aged<br>16<br>Days) |     |     |        | 1857.4 |

|    |               |          |                                 |     |     |        |  |
|----|---------------|----------|---------------------------------|-----|-----|--------|--|
| 64 | Titania       | Dopamine | Base<br>(Ammonium<br>Carbonate) |     |     |        |  |
| 65 | Titania       | Dopamine | Base<br>(Ammonium<br>Carbonate) |     |     | Cu(II) |  |
| 66 | Maringa       | Dopamine |                                 |     |     |        |  |
| 67 | Maringa       | Dopamine | Base                            |     |     |        |  |
| 68 | Cocoa<br>Husk | Dopamine |                                 |     |     |        |  |
| 69 | Cocoa<br>Husk | Dopamine | Base                            |     |     |        |  |
| 70 |               | Dopamine |                                 |     |     |        |  |
| 71 |               | Dopamine | Base                            |     |     |        |  |
| 72 |               | Dopamine | Base                            | BSA |     |        |  |
| 73 |               | Dopamine | Base                            | BSA | DNA |        |  |
| 74 |               | Dopamine | Base                            | BSA | DNA | Cu(II) |  |
| 75 |               | Catechol |                                 |     |     |        |  |
| 76 |               | Catechol | Base                            |     |     |        |  |
| 77 |               | Catechol | Base                            | BSA |     |        |  |
| 78 |               | Catechol | Base                            | BSA | DNA |        |  |
| 79 |               | Catechol | Base                            | BSA | DNA | Cu(II) |  |
| 80 |               | Water    |                                 |     |     |        |  |
| 81 |               | Water    | Base                            |     |     |        |  |
| 82 |               | Water    | Base                            | BSA |     |        |  |
| 83 |               | Water    | Base                            | BSA | DNA |        |  |
| 84 |               | Water    | Base                            | BSA | DNA | Cu(II) |  |
| 85 | Zeolite       |          |                                 |     |     | Cu(II) |  |
| 86 | Zeolite       |          |                                 |     | DNA | Cu(II) |  |
| 87 | Zeolite       | Dopamine |                                 |     | DNA | Cu(II) |  |
| 88 | Zeolite       | Dopamine |                                 | BSA | DNA | Cu(II) |  |
| 89 | Zeolite       | Dopamine | Base                            | BSA | DNA | Cu(II) |  |
| 90 | Zeolite       |          |                                 |     |     | Cu(II) |  |
| 91 | Zeolite       |          |                                 |     | DNA | Cu(II) |  |
| 92 | Zeolite       | Catechol |                                 |     | DNA | Cu(II) |  |
| 93 | Zeolite       | Catechol |                                 | BSA | DNA | Cu(II) |  |
| 94 | Zeolite       | Catechol | Base                            | BSA | DNA | Cu(II) |  |
| 95 | Zeolite       |          |                                 |     |     | Cu(II) |  |
| 96 | Zeolite       |          |                                 |     | DNA | Cu(II) |  |
| 97 | Zeolite       | Water    |                                 |     | DNA | Cu(II) |  |
| 98 | Zeolite       | Water    |                                 | BSA | DNA | Cu(II) |  |
| 99 | Zeolite       | Water    | Base                            | BSA | DNA | Cu(II) |  |

**[00124]** Immediately after the synthesis of each material, the samples were frozen at -80 degrees Celsius and then lyophilized. Examples of actual yields for any permutation may also be found in Table 1. Typically, the yields were 90-100% of the theoretical yield.

**[00125]** Mild steel coupon panels (12" by 4") were primed with the SigmaGlide 200 Primer/Hardener (PPG) system via spray, roller, or brush application and allowed to cure at room temperature for two to three days. Subsequently, a "Tie" Layer was applied (Sigma Glide 700 Primer/Hardener System, PPG) again utilizing spray, roller, or brush application, and allowed to cure at room temperature for 2-3 days. The "Tie" Layer is required for adhesion of the superficial topcoat layer due to the prevalence of PDMS and other silicon-containing components in the topcoat (SigmaGlide 1200, PPG).

**[00126]** The SigmaGlide System is characterized as a "Foul-Release" Marine Paint and does NOT incorporate any biocides, although the curing system for the Top Coat (SigmaGlide 1200) utilizes a tin(IV)-based catalyst which may remain in the coating even after completion of the curing process.

**[00127]** Sixty formulations were chosen for application to the Mild Steel Coupons for field deployment (Formulations 1-60 in Table 1). Typically, 100 mg of each individual material lyophile was finely milled and then added to 2-4 mL of SigmaGlide 1200 Topcoat, followed by the addition of SigmaGlide 1200 Hardener (at 25% v/v of SigmaGlide 1200 Topcoat). The weight percent of materials 1-60 relative to the mass of the solids in the SigmaGlide 1200 Topcoat ranged from 1-50%. All materials dispersed easily into the SigmaGlide 1200 Topcoat. Subsequent to curing at room temperature for 2-3 days, no difference in tack was evident for any test coating relative to the SigmaGlide 1200 controls.

**[00128]** Each sample was vigorously mixed via mechanical agitation for approximately 2-3 minutes, and then applied via individual disposable brushes to the Mild Steel Coupons (previously coated with cured SigmaGlide 200 Primer and SigmaGlide 700 Tie Layer Systems) as individual 1 inch X 1 inch squares. Customized stencils allowing for 30 1" by 1" paint squares per panel (10 squares by 3 squares) were applied to the coupons prior to the addition of the Top Coat

(SigmaGlide 1200) to ensure uniformity and allow for similar uncoated distances and areas (i.e., exposed Tie Layer) between the 1" by 1" painted squares.

**[00129]** Each treated panel contains both control samples (SigmaGlide 1200 Top Coat only, without test material additives) and experimental samples (SigmaGlide 1200 Top Coat with test material additives) in a randomized grid with at least 4 replicates of any given sample, whether control or experimental. The randomized grid was custom-designed to control for the location on the Mild Steel Coupon of each particular square with regard both to height (top-to-bottom) and adjacency of other painted squares (i.e., the number of neighboring squares). Each panel accommodates SigmaGlide 1200 controls and six individual test material-doped SigmaGlide 1200 samples. The dimensions and spatial arrangement of the thirty squares/panel are shown in FIG. 2.

**[00130]** For each of the two deployment sites, 10 Mild Steel Panels (as described above) were required to accommodate the sixty distinct test materials chosen for deployment (i.e., samples 1-60 from Table 1). For each deployment site, the ten coated Mild Steel Coupons were bolted to a propeller-shaped rig constructed from pressure-treated wood. Rope lines were threaded through the centers of each rig (from top to bottom) with sufficient space to allow for free rotation of the rig about the central axis defined by the rope. The entirety of each rig was then suspended within a steel cage of sufficient length, width, and height to allow for the maintenance of free rotation about the central axis within the cage. The cage was employed to prevent any mechanical damage to the coated panels from any floating or neutrally-buoyant detritus which may be present in the natural waterways of the chosen deployment sites. The cages were then sunk to the bottom of the natural waterway and allowed to incubate (i.e., biofoul) for approximately 14 weeks, at which point they were pulled to the surface, imaged, and evaluated for fouling by various marine species. At the Highland Beach site, the panels were rinsed using a low-velocity water mist, and then re-imaged. After imaging, the rigs were re-deployed to the seafloor to allow for further fouling.

**[00131]** The two sites selected for deployment were in the Florida Intracoastal Waterway. The first site was Highland Beach, FL and the second site was Pompano Beach, FL. The first site was chosen for proximity to the main Intracoastal Channel

(i.e., proximity to the Atlantic Ocean) and the second site was chosen owing to its greater distance from the main Intracoastal Channel. Additionally, the first site (Highland Beach) is located in a “dead-end” waterway characterized by a low (tide-dependent) water flux whereas the second site (Pompano Beach) is located in a more open environment with significantly greater water flux.

**[00132]** In addition to the panels described above, ten materials, as described in Table 2, were chosen for “whole-panel” application, mixed with the SigmaGlide 1200 TopCoat and applied to the entirety of the fronts of ten individual Mild Steel Coupon Panels and deployed on the same rig at the Highland Beach site of the Florida Intracoastal Waterway. This rig was deployed “freely” and did not have the mechanical protection of a surrounding steel cage as was applied to the first deployment, but was able to rotate freely about the central rope axis.

Table 2

| <b>Sample ID#</b> | <b>Particulate</b> | <b>Active</b> | <b>Base</b> | <b>BSA</b> | <b>DNA</b> | <b>Cu(II)</b> |
|-------------------|--------------------|---------------|-------------|------------|------------|---------------|
| 61                | Bentonite          | Dopamine      | Base        |            |            |               |
| 62                | Bentonite          | Dopamine      | Base        | BSA        |            |               |
| 63                | Bentonite          | Dopamine      | Base        | BSA        | DNA        | Cu(II)        |
| 64                | Bentonite          | Dopamine      | Base        | BSA        | DNA        |               |
| 65                | Lignin             | Dopamine      | Base        |            |            |               |
| 66                | Titanium           | Dopamine      | Base        |            |            |               |
| 67                | Zeolite            | Dopamine      | Base        |            |            |               |
| 68                | Maringa            | Dopamine      | Base        |            |            |               |
| 69                | Cocoa Husk         | Dopamine      | Base        |            |            |               |
| 70                | Control            |               |             |            |            |               |

**[00133]** A second marine paint system (ABC4, PPG), characterized as an “Ablative” Marine Paint and containing as much as 40% Copper (I) Oxide by weight, was also employed as a base paint for the test material additives. The panels were again primed with the SigmaGlide 200 system prior to applying the top coat, and the test materials were added at 1-50% wt/wt solids relative to the ABC4 formulation.

**[00134]** The protocol for inclusion of the additives is identical to that utilized for the SigmaGlide system described above, and the same sixty library members were applied to Mild Steel Coupons using the same statistical design and layouts described above and deployed at the same two sites in the Florida Intracoastal Waterway utilizing the protective steel cages about the freely-rotating pressure-treated wood rigs.

**[00135]** As was the case for the SigmaGlide system, each test material was easily wetted in the ABC4 formulation and dispersed uniformly throughout the pre-cured paint system.

**[00136]** In addition to the paint formulations described above, various materials of the type disclosed herein were successfully dispersed into and cured using a variety of commercial systems including alkyds, epoxys, acrylics, polyurethanes, and various "mixed" systems. Additionally, the test materials were successfully incorporated into lab-based coating formulations. As a non-limiting example, well-dispersed and non-tacky formulations utilizing a bisphenol A diglycidyl ether epoxy system with either 1,2-diaminoethane or 1,6-diaminohexane as the cross-linker/hardener are easily formulated and applied to a variety of surfaces.

**[00137]** Ropes of various materials (polypropylene, nylon, sisal, and jute) as well as PVC screens were also coated with the materials IN THE ABSENCE of any paints or other coating system components and exhibited anti-fouling properties well in excess of the untreated controls.

#### STATEMENTS REGARDING INCORPORATION BY REFERENCE AND VARIATIONS

**[00138]** All references cited throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is

partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

**[00139]** The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the invention has been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed can be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the invention and it will be apparent to one skilled in the art that the invention can be carried out using a large number of variations of the devices, device components, and method steps set forth in the present description. As will be apparent to one of skill in the art, methods and devices useful for the present methods and devices can include a large number of optional composition and processing elements and steps. All art-known functional equivalents of materials and methods are intended to be included in this disclosure. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

**[00140]** When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure.

**[00141]** It must be noted that as used herein and in the appended claims, the singular forms "a", "an", and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to "a molecule" includes a plurality of such molecules and equivalents thereof known to those skilled in the art, and so forth. As well, the terms "a" (or "an"), "one or more" and "at least one" can be used interchangeably herein. It is also to be noted that the terms "comprising",

"including", and "having" can be used interchangeably. The expression "of any of claims XX-YY" (wherein XX and YY refer to claim numbers) is intended to provide a multiple dependent claim in the alternative form, and in some embodiments is interchangeable with the expression "as in any one of claims XX-YY."

**[00142]** 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 to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are described.

**[00143]** Whenever a range is given in the specification, for example, a range of integers, a temperature range, a time range, a composition range, or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. As used herein, ranges specifically include the values provided as endpoint values of the range. As used herein, ranges specifically include all the integer values of the range. For example, a range of 1 to 100 specifically includes the end point values of 1 and 100. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

**[00144]** As used herein, "comprising" is synonymous and can be used interchangeably with "including," "containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" can be replaced with either of the other two terms. The invention illustratively described herein suitably can be practiced in the absence of any element or elements, limitation or limitations which is/are not specifically disclosed herein.

## CLAIMS

What is claimed is:

1. An anti-fouling and/or foul-releasing composition comprising:  
a crosslinked polyhydroxyaromatic polymer; and  
a biopolymer at least partially encapsulated by the crosslinked polyhydroxyaromatic polymer.
2. The anti-fouling and/or foul-releasing composition of claim 1, wherein monomers for forming the polyhydroxyaromatic polymer are selected from the group consisting of catechol, quinones, hydroquinones, dopamine, norepinephrine, epinephrine, catecholamines, catecholic amino acids, indoles, naphthalenes and combinations thereof.
3. The anti-fouling and/or foul-releasing composition of claim 1, wherein crosslinking agents for crosslinking the polyhydroxyaromatic polymer are selected from the group consisting of bifunctional alkanes, bifunctional amines, trifunctional amines, trifunctional silanes, thiol-based crosslinkers and combinations thereof.
4. The anti-fouling and/or foul-releasing composition of claim 1, wherein the biopolymer is selected from the group consisting of double-stranded DNA, single-stranded DNA, serum albumins, hemoglobin, carbohydrates, saccharides and combinations thereof.
5. The anti-fouling and/or foul-releasing composition of claim 1, wherein at least a portion of the biopolymer is cleaved from the anti-fouling composition by hydrolytic enzymes secreted by bacteria.
6. The anti-fouling and/or foul-releasing composition of claim 5, wherein bacterial matter replaces at least a portion of the biopolymer cleaved from the anti-fouling and/or foul-releasing composition, thereby regenerating the anti-fouling composition.

7. The anti-fouling and/or foul-releasing composition of claim 1, wherein a concentration of the biopolymer is between 0.5% w/w and 25% w/w.
8. The anti-fouling and/or foul-releasing composition of claim 1, wherein at least a portion of the crosslinked polyhydroxyaromatic polymer and/or the biopolymer is bound to a metal ion.
9. The anti-fouling and/or foul-releasing composition of claim 8, wherein the metal ion is selected from the group consisting of  $\text{Cu}^{2+}$ ,  $\text{Cu}^+$ ,  $\text{Pb}^{4+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Hg}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Cd}^+$ ,  $\text{Ag}^+$ ,  $\text{As}^{3+}$ ,  $\text{As}^{5+}$  and combinations thereof.
10. The anti-fouling and/or foul-releasing composition of claim 1 further comprising a structural material.
11. The anti-fouling and/or foul-releasing composition of claim 10, wherein the structural material is selected from the group consisting of lignin, titanium dioxide, silica, bentonite clay, calcium carbonate, corals, zeolite, polyethyleneglycol (PEG) and combinations thereof.
12. The anti-fouling and/or foul-releasing composition of claim 1, wherein the anti-fouling composition is formed as a film, an aggregate, a powder, a microparticle, a nanoparticle, a core-shell particle or a combination thereof.
13. The anti-fouling and/or foul-releasing composition of claim 1, wherein the anti-fouling and/or foul-releasing composition is a component of a product or a stand-alone coating.
14. The anti-fouling and/or foul-releasing composition of claim 1 further comprising an additive selected from the group consisting of surfactants, wetting agents, opacifiers, waxes, slip agents, drying rate modifiers, surface tension modifiers, matting agents, leveling agents, UV stabilizers, pigments and combinations thereof.

15. A product comprising the anti-fouling composition of any one of the preceding claims.
16. A method of using an anti-fouling and/or foul-releasing composition, comprising:  
  
applying the anti-fouling composition of any one of claims 1-15 to at least a portion of a substrate; and  
  
exposing the portion of the substrate to a fresh or salt water environment.
17. The method of claim 16, wherein the substrate comprises a material selected from the group consisting of metal, plastic, fiberglass, rubber, ceramic, wood, flora, fauna and combinations thereof.
18. The method of claim 16, further comprising mixing the anti-fouling and/or foul-releasing composition with an adhesive prior to applying the anti-fouling composition to the substrate.
19. The method of claim 16, wherein the step of applying comprises forming the anti-fouling composition as a film on the substrate.
20. The method of claim 16, wherein the step of applying comprises painting, spraying or drop coating a formulation comprising the anti-fouling composition onto the substrate.
21. A method of making an anti-fouling and/or foul-releasing composition, comprising:  
  
dispersing a polyhydroxyaromatic monomer, a crosslinking agent, and a biopolymer in a solvent.
22. The method of claim 21 further comprising dispersing a structural material in the solvent.

23. The method of claim 21 or claim 22, wherein the solvent has a pH between 3.5 and 11.5.
24. The method of claim 21 or claim 22, wherein the components are added to the solvent sequentially or simultaneously.

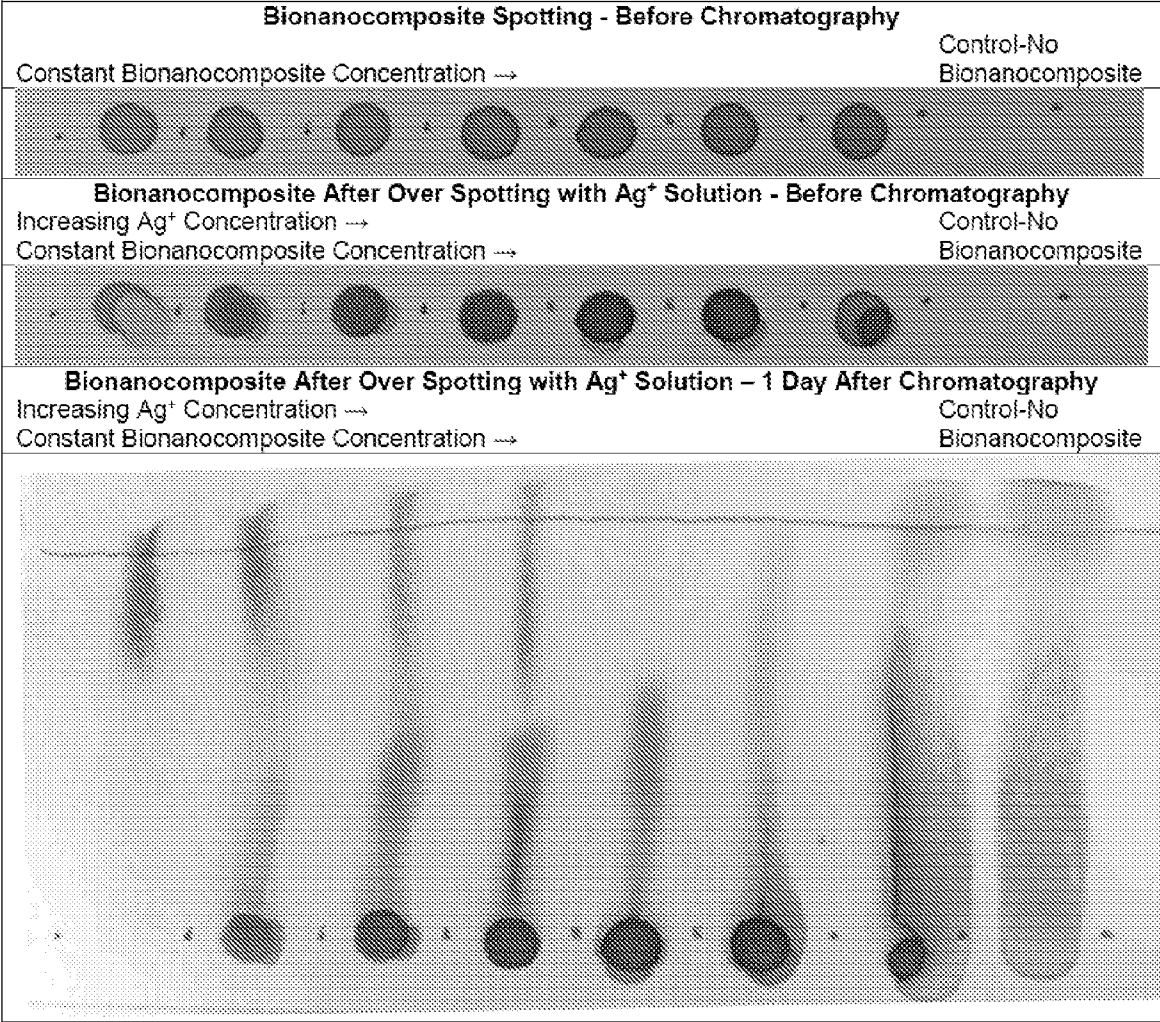


FIG. 1

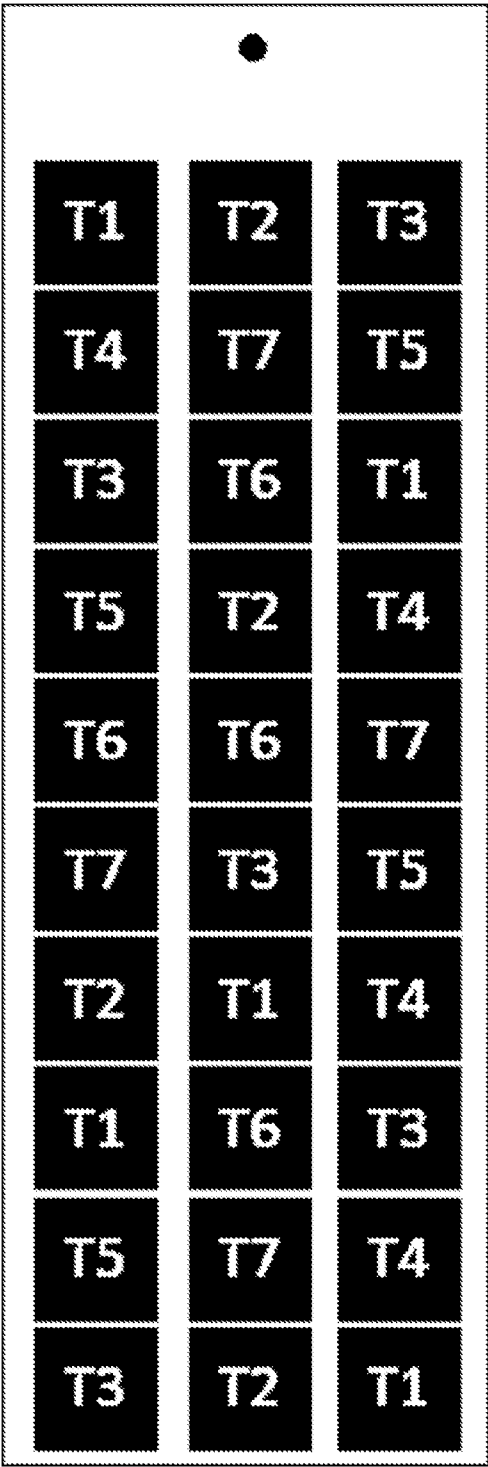


FIG. 2

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 21/42113

## A. CLASSIFICATION OF SUBJECT MATTER

IPC - G01N 21/78; G01N 33/52; G01N 31/22 (2021.01)

CPC - G01N 21/78; G01N 31/22; G01N 33/0098; G01N 33/52

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)

See Search History document

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

See Search History document

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

See Search History document

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category*     | Citation of document, with indication, where appropriate, of the relevant passages                                                        | Relevant to claim No.  |
|---------------|-------------------------------------------------------------------------------------------------------------------------------------------|------------------------|
| X<br>---<br>Y | US 2017/0266353 A1 (DSM IP Assets B.V.) 21 September 2017 (21.09.2017) - entire document especially para[0007], [0013], [0061] and [0069] | 1-15<br>-----<br>21-24 |
| Y             | US 2015/0191607 A1 (Reactive Surfaces LTD) 09 July 2015 (09.07.2015) - entire document especially para[0022], [0048] and [0515]           | 21-24                  |
| A             | US 2019/0000909 A1 (LiveLeaf Inc) 03 January 2019 (03.01.2019) - entire document                                                          | 1-15, 21-24            |
| A             | WO 2013/120009 A1 (Georgia-Pacific Chemicals LLC) 15 August 2013 (15.08.2013) - entire document                                           | 1-15, 21-24            |
| A             | US 2018/0371248 A1 (Momentive Performance Materials GmbH) 27 December 2018 (27.12.2018) - entire document                                 | 1-15, 21-24            |

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

\* Special categories of cited documents:

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

"D" document cited by the applicant in the international application

"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

28 September 2021

Date of mailing of the international search report

**OCT 26 2021**

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. 571-273-8300

Authorized officer

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Telephone No. PCT Helpdesk: 571-272-4300

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 21/42113

## 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.: 16-20  
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:

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.:

### 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.