

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
24 February 2005 (24.02.2005)

PCT

(10) International Publication Number
WO 2005/017051 A2

(51) International Patent Classification⁷: **C09D**

(21) International Application Number:
PCT/US2004/026515

(22) International Filing Date: 13 August 2004 (13.08.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/495,046 14 August 2003 (14.08.2003) US
60/496,996 21 August 2003 (21.08.2003) US

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,
FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI,
SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: PAINTS, COATINGS AND POLYMERS CONTAINING PHYTOCHEMICAL AGENTS AND METHODS FOR MAK-
ING AND USING SAME

(57) Abstract: The present invention provides safe paint and coating compositions comprising at least one environmentally ac-
ceptable phytochemical such as, but not limited to capsicum, grapefruit seed extract and menthol suitable for use in preventing the
colonization of a treated surface by a variety of biological species. One aspect of the invention is anti-fouling marine paints (coat-
ings). Another aspect of the invention of the present invention provides paint and coating compositions comprising phytochemicals
for use as an architectural paint. The compositions of the invention can further comprise control release agents such as, for exam-
ple, antioxidants, oxidizers or photosensitive compounds to promote sustained release of the anti-colonization agents at the treated
surface and to assist in the abrasion of the paint surface to mechanically dislodge the attaching organisms.



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**PAINTS, COATINGS AND POLYMERS CONTAINING PHYTOCHEMICAL
AGENTS AND METHODS FOR MAKING AND USING SAME**

Field of the Invention

This invention relates generally to coatings including marine and architectural paints
5 containing one or more phytochemical agents for use in inhibiting the colonization of treated
surfaces by animals and/or plants.

Background of the invention

Historically, toxic chemicals, including the salts and oxides of heavy metals, have
been added to marine paints to control fouling caused by the build up of plant and animal
10 organisms on marine vessel hull bottoms and structures. This marine fouling can seriously
diminish the performance of a ship's hull through the water, as well as causing structural
damage. Both marine and freshwater vessels are susceptible to bottom fouling that can result
in significant economic penalties.

Phytochemicals are known which have broad activity, preventing or inhibiting the
15 growth of a broad spectrum of microbes, as well as exhibiting efficacy against a range of
potential marine fouling organisms such as, for example, barnacles, tubeworms and algae.
For example, phytochemicals have been incorporated into polymeric films useful for
wrapping and protecting foodstuffs during storage as described in U.S. Patent Serial Number
5,906,825. Capsicum, at high pungency levels, has been added to marine paints to prevent
20 the fouling of ships bottoms, as described in U.S. Patent Serial Number 5,397,385. However,
while showing efficacy against hard fouling by barnacles and mussels, there is limited effect
in controlling soft fouling such as by algae. There is still an unmet need, therefore,
treatments that can reduce or eliminate hard and soft fouling of submerged marine surfaces,
as well as attachment and growth of drier surfaces by such as mildew, for example.

25 Phytochemicals that leach out of paint dilute and disperse extremely well into water
and their biodegradability environmental acceptability. Their anti-fouling effect particularly
resides in a surface effect that takes place only in the immediate environment of the painted
or coated surface. This characteristic makes the compositions of the present invention
comprising phytochemicals compatible with leaching coatings, ablative coatings and self-
30 polishing coatings (polymers).

A need still exists, however, for safe, environmentally friendly alternatives to toxic
additives in marine paints and architectural coatings that may be harmful to the applicant of
the paint or to individuals who may come into direct contact with a treated surface.

Summary of the Invention

The present invention recognizes and addresses the foregoing disadvantages, and others of prior art constructions and methods. The present invention provides safe paint and coating compositions comprising at least one environmentally acceptable phytochemical suitable for use in preventing the colonization of a treated surface by a variety of biological species. One aspect, therefore, of the invention is anti-fouling marine paints (coatings). Another aspect of the invention of the present invention provides paint and coating compositions comprising phytochemicals for use as an architectural paint, including alkyl, polyvinyl acetate emulsion, polyvinyl chloride emulsion, water based epoxy resin, acrylic emulsion, acrylic resins, copolymers, synthetic composites, vinyls and other types of siding and derivatives thereof. The compositions of the invention can further comprise control release agents such as, for example, vitamin E or oxidizers or photosensitive compounds to promote sustained and release of the anti-colonization agents at the treated surface and to assist in the abrasion of the paint surface to mechanically dislodge the attaching organisms.

In one embodiment of the present invention, the phytochemicals can be active in the inhibition or control of hard marine fouling (e.g. barnacles) and soft fouling (for example by algae) or a phytochemical may only be active against one type of fouling, and therefore a combination of phytochemicals is required to achieve efficacy.

In various embodiments of the invention, the phytochemical capsicum is combined with one or more other phytochemicals and added to a marine paint or coating to control marine fouling. In other embodiments of the invention, the phytochemical capsicum is combined with one or more other phytochemicals and added to an architectural paint or coating to control biological colonization (fungal, algal or bacterial attachment) of an architectural painted surface. In one embodiment, the phytochemical, capsicum may be combined with other phytochemicals and added to marine paint to control marine fouling, wherein the capsicum is substantially free of the heat causing ingredient capsaicin.

The phytochemical can be added to architectural and marine paints alone or in combination with other phytochemicals, or in combination with antioxidants such as Vitamin E or oxidizers or photosensitive compounds suitable for chemically disrupting the outer surface of the applied paint. In an alternative embodiment, the phytochemical camphor is used in combination with other phytochemicals as a marine organism-fouling preventive. Camphor is a crystalline ketone derived from the wood of the camphor tree *Cinnamomum camphora*.

In one embodiment of the compositions of the present invention, the phytochemical combination comprises a capsicum preparation and tannic acid, and menthol or a derivative thereof. In another embodiment, the phytochemical combination comprises capsicum, tannic acid, clove oil, garlic and menthol. In yet another embodiment the phytochemical combination comprises a capsicum preparation, tannic acid, garlic and clove oil.

In one embodiment of the compositions of the present invention, the phytochemical combination comprises a capsicum preparation and tannic acid, and menthol or a derivative thereof. In another embodiment, the phytochemical combination comprises capsicum, tannic acid, clove oil, garlic, rosemary, sage, bayleaf, oregano and menthol. In yet another embodiment the phytochemical combination comprises a capsicum preparation, tannic acid, garlic and clove oil. In one embodiment of the paints and coatings of the present invention, the phytochemical combination comprises capsicum and clove oil and optionally garlic. In another embodiment the phytochemical combination comprises capsicum, clove oil, garlic and *Zostera noltii* (eel grass), with or without vitamin E. In one embodiment the phytochemical combination comprises capsicum, tannic acid, menthol and *Zostera noltii* (eel grass),. In still another embodiment the phytochemical combination comprises a capsicum preparation, menthol, grapefruit seed extract and *Zostera noltii* (eel grass),. In still another embodiment of the invention, the phytochemical combination comprises a capsicum preparation, menthol, grapefruit seed extract, neem oil and *Zostera noltii* (eel grass),. In yet another embodiment, the phytochemical combination comprises a capsicum preparation, menthol, and neem oil.

In embodiments of the paints and coatings of the present invention, phytochemicals of the present invention may be added in any combination to leaching paints (hard and soft), ablative paints (coatings), self-polishing coatings (polymers), longlife anti-fouling coatings and fouling-release coatings, at levels from about .01% to about 60% by volume or weight to weight. In other embodiments of the paints and coatings of the present invention, phytochemicals of the present invention may be added in any combination to leaching paints (hard and soft), ablative paints (coatings), self-polishing coatings (polymers), longlife anti-fouling coatings and fouling-release coatings, at levels from about .01% to about 50% by volume or weight to weight.

Detailed Description of the Invention

The present invention provides paint and coating compositions comprising environmentally benign phytochemicals suitable for use in preventing the colonization of a

treated surface by various biological species. One aspect, therefore, of the invention is anti-fouling marine paints (coatings). Another aspect of the invention of the present invention provides paint and coating compositions comprising phytochemicals for use as architectural paints, alkyl, polyvinyl acetate emulsion, polyvinyl chloride emulsion, water based epoxy resin, acrylic emulsion, acrylic resins, copolymers, synthetic composites, vinyls and other types of siding and derivatives thereof.

Definitions

The term "paint base" as used herein refers to a mixture of a polymeric primer, and a suitable solvent or suspension medium. It will be understood by one of skill in the art that the paint base is suitable for application to the submerged hull of a ship or boat, water intake and discharge systems for reservoirs and nuclear power plants (a marine paint base) and/or to the surface of, for example, a building or article of furniture (an architectural paint) and will provide a durable coating thereof. The paint may be an ablative paint wherein the immediate outer surface of the applied paint coating may be removed by frictional forces as a hull moves through water. The ablation will contribute to the mechanical removal of any colonizing organisms, as well as maintain the effective concentration of the phytochemical at the immediate surface. An ablative paint may include, for example, zinc oxide that provides a surface that may be sloughed off by the frictional action of water against the hull surface. It is contemplated, however, that the paint base for use in the compositions of the invention may comprise an oxidant that may disrupt the chemical structure of the exposed paint surface thereby allowing this surface to be removed by mechanical means such as wiping or by water jet or spray. Oxidative or photochemical breakdown of the paint surface is of particular use in architectural paints that are not subject to the continuous abrasive action of water over the treated surface. Suitable paint bases for use in the present invention include, but are not limited to an epoxy based paint, a silicone based paint, a polyurea resin, an alkyl, a polyvinyl acetate emulsion, a polyvinyl chloride emulsion, a water based epoxy resin, an acrylic emulsion, an acrylic resin, a copolymer, a synthetic composite, a vinyl, an ablative paint, a self-polishing paint, a leaching paint, a non-leaching paint, an oil-based paint, an aqueous-based paint and derivatives thereof.

The term "primer" as used herein refers to, but is not limited to, chlorinated natural rubber primer, epoxy resin primers, silicone elastomer primer, and epoxy polysiloxane.

The term "resin" as used herein refers to, but is not limited to, polysulfonates, silyl ether polymers, urea-based resins and polyphosphates.

The term "pigment" as used herein refers to, but is not limited to, calcium carbonate, zinc oxide, iron oxide).

The term "solvent" as used herein refers to, but is not limited to, xylene, methyl isobutyl ketone, organic solvent including, but not limited to, acetone, turpentine and synthetic paint solvent. An acrylic based paint or medium may have as a solvent an aqueous based medium that may comprise other solvents including, for example, isopropanol.

The terms "binder" and "fouling control agent" as used herein refers to, but is not limited to, rosins, resins, acrylic siloxine, acrylic-siloxine graft copolymers, calcium carbonate, siloxanes, silicones, silylacrylates, hydrolysable; trimethylsilyloxyethyl methacrylate copolymer; the copolymers, methyl acrylate, methyl methacrylate, styrene, lauryl methacrylate, vinyl acetate, vinyl chloride, acrylate copolymer paint binders and ester terminated silicones.

The term "anti-settling agent" as used herein refers to, but is not limited to, polyamide wax, paraffin waxes and hydrocarbon waxes.

The term "marine" as used herein refers to any aqueous environment including sea and freshwater either in the open environment such as the ocean, a lake or river, or any other extensively submerged surface such as the lining of a pipe or the inner surface of a fish tank, a water intake and discharge systems for reservoirs, for example.

The term "colonization" as used herein refers to the attachment of organisms to a surface. The attachment may result in the subsequent growth and proliferation of the organism on the surface.

The term "active concentration" as used herein refers to the concentration of the phytochemical agents available for exhibiting control of marine organism growth on surfaces below the water. For application in ablative paint (coatings), self-polishing coatings, longlife coatings and fouling release coatings the present invention, using phytochemicals alone or in combination, with or without migration control agents, active concentration levels of the phytochemical concentrations will repel or inhibit the growth of marine organisms on underwater surfaces that are safe for the environment.

The term 'phytochemicals' is herein defined to include complete, naturally occurring phytochemical molecular constructions, derivatives thereof, functional moieties thereof, and functionally identical manufactured molecular constructions as may be obtained based upon the naturally occurring compositions herein described. The term "phytochemical" as used herein refers to a compound or combination of compounds isolated from botanical sources and which may be incorporated in the present invention include, but are not limited to,

Jasonia candicans (sesquiterpenes, lactones); *Polygonum flaccidum* (flavone and alpha santalene derivatives); *Acalypha wilkesiana* (extracts); *Pavetta owariensis* (procyanidins); *Plectranthus hereroensis* (diterpenoids, diterpenes); Moss (Dicranin extract); *Cannabis sativa* (extract); *Gloiosiphonia* spp. (gloiosiphones); *Laminaceae* spp. (extract); *Securidaca* spp.
 5 (extract); *Veronia* spp. (extract); *Hyptis umbrose* (umbrosone); *Asclepias syriaca* (milkweed extract); *Tagetes tenuifolia* (thiophene); *Calophyllum inophylloide* (flavonoids); *Tanacetum densum* (sesquiterpene lactones, triterpenoids); *Neorautanenia mitis* (extract); *Premna schimper* (diterpene); *Premna oligotricha* (sesquiterpenes); *Premna oligotricha* (diterpenes); *Jasonia candicans* (essential oils); *Visnea mocanera* (beta-sitosterol, triterpenic betulinic
 10 acid, ursolic acid, plantanic acid); *Asteraceae* spp. (terthiophenes and polyynes); *Petalostemum purpureum* (extract); *Camelia sinensis* (catechin); *Helichrysum picardii* (flavonoids); *Helichrysum italicum* (flavonoids); *Corydalis pallida* (protoberberine alkloids); *Shiraa bambusicola* (perylenequinones); *Fraxinum omus* (hydroxycoumarins); *Podocarpus nagi* (tatarol and nortiterpene dilactones); *Heterotheca inuloides* (sesquiterpenoids);
 15 *Pelargonium* spp. (essential oils); *Piper sarmentosum* (phenylpropanoids); *Allium* spp. (extract); *Juniperus procera* (diterpenes); *Achillea conferta* (flavonoids, flavones, sesquiterpenoid lactones); *Magnolia virginiana* (lignans, neolignans); *Eucalyptus euglobal* (euglobal); *Armillaria mellea* (armillaric acid); *Dracena mannii* (spirostanol saponin); *Piper aduncum* (chromenes, prenylated benzoic acid); *Rhamnaceae* spp. (cyclopeptide alkaloids);
 20 *Buddleja globosa* (verbascoside); *Cephalocereus senilis* (phytoalexin aurone); *Salvia albocaerulea* (diterpene); *Gomphrena martiana* and *Gomphrena boliviana* (extracts); *Paepalanthus* spp. (vioxanthin); *Helichrysum stoechas* and *Helichrysum crispum* (extracts); *Achillea ptarmica* (trans-pinocarveyl hydroperoxides); *Dehaasia incrassata* (alkaloids); *Asteraceae* spp. (extracts); *Arctotis auriculate* (extracts); *Eriocephalus africanus* (extracts):
 25 *Felicia erigeroides* (extracts); *Hemerocallis fulva* (phytosterols, fatty acid esters); *Psoralea juncea* (plicatin B); *Pluchea symphytifolia* (caffeic acid esters); *Tovomitopsis psychotrifolia* (Vitamin E derivative); *Celosia argentea* (triterpenoid saponins and flavonoids); *Azadirachta indica* (tetranortriterpenoid, mahmoodin, protolimonoids, naheedid); *Moraceae* spp. (coumarins); *Hypericum erectum* (phloroglucinol derivatives); *Podospora appendiculate*
 30 (Appenolides A, B, & C, furanones); *Artemisia princeps* var. *orientalis*, *Artemisia capillaris*, *Artemisia mexicana* and *Artemisia scoparia* (extract); Paddy malt (mash extract); *Kigelia pinnata* (extract); *Acalypha wilkesiana* (extract); seaweeds, seagrass and lemongrass (essential oils); *Borrieria latifolia*, *Borreria setidens*, *Hedyotis diffusa*, *Hedyotis nudicaulis*, *Morinda elliptica*, *Morinda umbellata*, *Sida rhombifolia*, and *Vitex ovata* (extracts); *Tabebuia*

impetiginosa, *Achyrocline* spp., *Larrea divaricata*, *Rosa borboniana*, *Punica granatum*,
Psidium guineense, *Lithrea ternifolia* (extracts); *Lepechinia caulescens*, *Lepidium virginicum*
 and *Tanacetum parthenium* (extracts); *Talaromyces flavus* (extracts); *Daucus carota*
 (extract); *Flabellia petiolata*, *Caulerpa prolifera*, *Halimeda tuna*, *Corallina elongata*,
 5 *Lithophyllum lichenoides*, *Phyllophora crispa*, *Cystoseira* spp., *Halopteris* spp., *Codium* spp.,
Valonia utricularis, *Posidonia oceanica*, *Zostera noltii* and *Cymodocea nodosa* (extracts);
Centauraea orientalis, *Diospyros khaki*, *Sida hermaphrodita*, *Forsythia intermedia*,
Scutellaria polydon, *Eugenia malaccensis* and *Eugenia jambolana* (extracts); *Fritillaria* L.
 spp. (ebeinone, steroidal alkaloids); *Kigelia pinnata*, *Peperomia pellucida*, *Populus nigra*,
 10 *Populus balsamifera* and *Populus deltoides* (extracts); *Melaleuca alternifolia* (essential oil);
Elfvigia applanata (naringenin); *Ficus sycomorus*, grapefruit seed, Garlic, *Allicin*, Peat,
Strophanthus hispidus, *Secamone afzeli*, *Mitracarpus scaber*, *Entada abyssinica*, *Terminalia*
spinosa, *Harrisonia abyssinica*, *Ximinea caffra*, *Azadirachta indica*, *Spilanthes mauritiana*,
Terminalia spinosa (extracts); Cyanobacteria (ambigols A and B, tjipanazole); coffee
 15 (extract); *Sporochmus pedunculatus*, *Dalbergia melanozylon*, *Celastrus scandens*, *Juglans*
nigra, *Kalmia latifolia*, *Pelargonium xhortorum*, *Rhus glabra* and *Lindera benzoin* (extracts);
Striga densiflora, *Striga orobanchioides*, *Striga lutea*, *Pistacia lentiscus* L., *Mitracarpus*
villosus, *Bixa orellana*, *Bridelia ferruginea*, *Alpinia katsumadai*, *Alpinia officinarum*,
Artemisia capillaris, *Casia obtusifolia*, *Dendrobium moniliforme*, *Epimedium grandiflorum*,
 20 *Glycyrrhiza glabra*, *Lithospermum erythrorhizon*, *Magnolia obovata*, *Morus bonbycis*,
Natopterygii incisium, *Polygonum multiflorum*, *Prunus mume*, *Rheum palmatum*, *Ricinus*
communis, *Sophora flavescens*, *Swertia japonica*, black pepper, rosemary, red pepper,
Isopyrum thalictroides, *Calotropis procera*, *Chrysanthemum* spp., *Holarrhena*
antidysenterica, *Lunularia crusiata*, *Dumertiera hirsuta*, *Exormothea tuberifera*, and
 25 liverwort (extracts); *Filipendula ulmaria*, *Salix glauca*, *Usnea filipendula*, *Clkadina*
arbuscula (salicylic compounds); *Tanacetum parthenium*, *Thymus capitatus*, and *Elfvigia*
applanata (extracts); *Fraxinus ornus* (hydroxycoumarins, esculin, esculetin, fraxin, and
 fraxetin); *Zizyphus nummularia*, LONGO VITAL, *Pelargonium* spp., *Scaevola sericea*,
Psychotria hawaiiensis, *Pipturus albidis*, *Aleurites moluccana*, *Solanum niger*, *Piper*
 30 *methysticum*, *Barringtonia asiatica*, *Adansonia digitata*, *Harungana madagascariensis*,
Jacaranda mimosaeifolia, *Erythroxylum catauba*, *Bidens pilosa*, *Lemna minor*, *Potamogeton*
 spp., *Nasturtium officinale*, *Apium nodiflorum*, *Agaricus subrutilescens*, *Amanita virosa*,
Amanita pantherina, *Lycoperdon perlatum*, *Psidium guajava*, *Averrhoa carambola*, *musa*
sapientum, *Carica papaya*, *Passiflora edulis*, *Lansium domesticum* and *Baccaurea motleyana*

(extracts); horse radish, celandine grass, bur marigold and yarrow grass (extracts); *Abuta grandifolia*, *Cyperus articulatus*, *Gnaphalium spicatum*, *Pothomorphe peltata*, *Ficus sycomorus*, *Ficus Benjamina*, *Ficus bengalensis*, *Ficus religiosa*, *Alchornea cordifolia*, *Bridelia feruginea*, *Eucalyptus citriodora*, *Hymenocardia acida*, *Maprounea africana*,
 5 *Monachora arbuscula*, *Tedania ignis*, *Arenosclera* spp., *Amphimedon viridis*, *Polymastia janeirensis*, *Aplysina fulva*, *Pseudaxinella lunaecharta*, *Nelumbium speciosum* and *Mycale arenosa* (extracts); cloves (eugenol acetate and iso-eugenol); *Chrysthaneum boreale* (sesquiterpenoid lactones); *Eucalyptus globulus*, *Punica granatum*, *Bocconia arborea*, *Syzygium brazzavillense*, *Syzygium guineense*, *Carthamus tinctorius*, *Ginkgo biloba*, *Mosla chinensis*, *Salvia officinalis*, and *Cinnamomum cassia* (extracts); *Cryptolepis sanguinolenta* (alkaloids, cryptolepine); *Chelidonium majus* (alkaloids, berberine, coptisine); *Vitex agnus-castus* (extract); *Cladonia substellata* (usnic acid); Ellagic acid, *Fuligo septica*, *Tubifera microsperma* (extract); *Mundulea monantha*, *Tephrosia linearis* (flavonoids); *Lpomoea fistulosa* (extract); *Pimenta dioica* (essential oils); *Ratibida latipalearis*, *Teloxys graveolens*,
 15 *Dodonaea viscosa*, *Hypericum calycinum*, *Hyptis albida*, *Hyptis pectinata*, *Hyptis suaveolens* and *Hyptis verticillata* (extracts); *Asteriscus graveolones* (bisabolone hydroperoxides); *Derris scandens*, *Alnus rubra*, *Araliaceae* family (extracts); *Vinca rosea*, Australian tea tree oil, peppermint oil, sage oil, thymol, eugenol and *Thuja orientalis* (extracts); *Anacardium occidentale* (phenolic lipids); *Oidiodendron tenuissimum* (extract); *Acacia nilotica* and
 20 *Acacia farnesiana* (polyphenol, tannin); *Teminalia alata* and *Mallotus phillipinensis* (extracts); *Piectranthus grandidentatus* (abientane diterpenoids); *Punica granatum* and *Datura metel* (extracts); tea, *Agave lecheguilla*, *Chamaesyce hirta*, *Baccharis glutinosa* and *Larrea tridentata* (extracts); *Camelia sinensis* and *Euphorbia hirta* (theaflavin, polyphenon 60); *Tabernaemontana pandacaqui*, *Yucca shidigera*, *Hemistepa lyrata*, *Yougia japonica*,
 25 *Prunella vulgaris*, *Lamium amplexicaule*, *Juniperus chinensis*, *Ixeris dentata*, *Gnaphalium affine*, *Chelidonium majus*, *Spirea prunifolia*, *Erythronium japonicum*, *Taxus wallichiana*, *Ganoderma lucidum* *Drava nemorosa*, *Youngia capillaris*, *Equisetum arvense*, Australian Lavender, Black Seed, *Catuaba casca*, *Cineole*, *Damiana*, *Dicranum scoparium*, Eucalptus oil, Ginger, and Grape seed (extracts); Neem seed, bark, and leaf extract; Neem oil; New
 30 Zealand Manuka extract; *Nicotiana tabacum* extract; olive leaf extract; a-pinene and b-pinene extracts; Rhubarb root extract; *Syringa vulgaris* extract; Tea tree oil (Terpinen-4-ol, a-terpinene, y-terpinene, a-terpineol, Terpinolene); Thyme (extract) and Vitamin E (extract).

Organisms inhibited by phytochemicals

Organisms which may be inhibited by phytochemicals useful in the present invention include, but are not limited to:

- Fungi: *Aspergillus flavus*, *A. fumigatus*, *A. niger*, *Blastomyces dermatitidis*, *Candida* spp., *Coccidioides immitis*, *Cryptococcus neoformans*, *Fusarium culmorum*, *Geotrichum* spp.,
- 5 *Histoplasma capsulatum*, *Malassezia furfur*, *Microsporum* spp., *Mucor racemosus*, *Nocardia* spp., *Paracoccidioides brasiliensis*, *Penicillium* spp., *Rhizopus higricans*, *Saccharomyces cerevisiae*, *Sporothrix schneckii*, *Torulopsis* spp., *Trichophyton* spp.
- Bacteria: *Aerobacter aerogenes*, *Aeromonas hydrophila*, *Bacillus cereus*, *Bacillus subtilis*, *Bordetella pertussis*, *Borrelia burgdorferi*, *Campylobacter fetus*, *C. jejuni*, *Corynebacterium*
- 10 *diphtheriae*, *C. bovis*, *Desulfovibrio desulfurica*, *Escherichia coli* 0157:H7, *Enteropathogenic E. coli*, *Enterotoxin-producing E. coli*, *Helicobacter pylori*, *Klebsiella pneumoniae*, *Legionella pneumophila*, *Leptospira interrogans*, *Mycobacterium tuberculosis*, *M. bovis*, *Neisseria gonorrhoeae*, *N. meningitidis*, *Proteus mirabilis*, *P. vulgaris*, *Pseudomonas aeruginosa*, *Rhodococcus equi*, *Salmonella choleraesuis*, *S. enteridis*, *S.*
- 15 *typhimurum*, *S. typhosa*, *Shigella sonnei*, *S. dysenteriae*, *Staphylococcus aureus*, *S. epidermidis*, *Streptococcus anginosus*, *S. mutans*, *Vibrio cholerae*, *Yersinia pestis*, *Y. pseudotuberculosis*, *Actinomycetes*, *Streptomyces reubrireticuli*, *Streptoverticillium reticulum*, *Thermoactinomyces vulgaris*
- Viruses: *Adenoviruses*, *Coronaviruses*, *Cytomegalovirus*, *Enteroviruses*, *Epstein-Barr virus*,
- 20 *Herpes simplex virus*, *Hepatitis viruses*, *Human Immunodeficiency virus*, *Human Parvoviruses*, *Influenza viruses*, *Morbillivirus*, *Mumps virus*, *Norwalk viruses*, *Papillomaviruses*, *Paromyxovirus*, *Poxvirus*, *Rabies virus*, *Reoviruses*, *Rotaviruses*, *Rubella virus*, *Respiratory Syncytial virus*, *Rhinoviruses*, *Varicella zoster virus*
- Parasites: *Ancylostoma braziliense*, *Anisakis*, *Babesia microti*, *Balantidium coli*, *Blastocystis*
- 25 *hominis*, *Chilomastix mesnili*, *Cryptosporidium parvum*, *Cyclospora*, *Dientamoeba fragilis*, *Diphyllobothrium latum*, *Echinococcus granulosus*, *Entamoeba coli*, *E. histolytica*, *Enterocytozoon*, *Fasciola hepatica*, *Giardia lamblia*, *Iodamoeba butschlii*, *Isospora belli*, *Leishmania brasiliensis*, *L. donovani*, *L. tropica*, *Paragonimus westermani*, *Plasmodium vivax*, *Pnemocystis carinii*, *Sarcocytis hominis*, *Strongyloides stercoralis*, *Taenia solium*,
- 30 *Toxoplasma gondii*, *Trichomonas vaginalis*, *Trichinella spiralis*, *Trypanosoma cruzi*.

It is further intended that the compositions of the present invention will be effective against marine and/or freshwater organisms capable of attaching to and colonizing the submerged hull surfaces of ships and boats, water intakes and discharge systems for reservoirs and nuclear power plants, including parazoans, coelenterates such as polychaete

and oligochaete worms, mollusks including zebra mussels, arthropods including crustaceans such as, but not limited to, acorn and goose barnacles and to be effective in inhibiting the attachment and or development of the adult or larval forms of the targeted organisms. The compositions of the present invention can also be effective against marine and freshwater plants including algae and higher plants that can attach to a ship hull and other underwater surfaces.

Exemplary phytochemicals which exhibit activity against multiple organisms are illustrated in Table 1 below. Each phytochemical is classified as to general activity (anti-bacterial; anti-viral; anti-fungal; anti-crustacean; larvicidal; insecticidal; molluscicidal; or anti-nematodal) and examples of organisms against which the phytochemical is active are provided. It should be recognized that the phytochemicals included in the table are for illustrative purposes only and are not meant to an exhaustive listing and with the recognition that certain phytochemicals may be active against more than one class of organism:

Table 1

Phytochemical	Known Target Organism
Anti-bacterial	
<i>Annona muricata</i> {Annonaceae}	<i>B. subtilis</i> ; <i>E. coli</i>
<i>A.squamosa</i>	<i>B. subtilis</i>
<i>Panax ginseng</i> {Araliaceae}	<i>E. coli</i> ; <i>P. aeruginosa</i> ; <i>S.enteritidis</i>
<i>Capparis spinosa</i> {Capparidaceae}	<i>E. coli</i>
<i>Calendula officinalis</i> {Compositae}	<i>B. subtilis</i> ; <i>S. lutea</i> ; <i>S. aureus</i>
<i>Cynara scolymus</i> {Compositae}	<i>E. coli</i>
<i>Cucurbita pepo</i> {Cucurbitaceae}	<i>S. aureus</i> ***
<i>Cymbopogon citratus</i> {Gramineae}	<i>B. subtilis</i> ; <i>B. mycoides</i> ; <i>S. aureus</i> ; <i>E. coli</i>
<i>Mentha spicata</i> {Labiatae}	<i>E. coli</i>
<i>Ocimum basilicum</i> {Labiatae}	<i>B. anthracis</i> ; <i>B. cereus</i> ; <i>S. aureus</i> ; <i>B. subtilis</i> ; <i>P. aeruginosa</i> ;
<i>Rosmarinus officinalis</i> {Labiatae}	<i>S. pneumoniae</i> ; <i>Actinomycetes</i>
<i>Glycyrrhiza glabra</i> {Leguminosae}	<i>B. subtilis</i> ; <i>B. cereus</i> ; <i>P. aeruginosa</i> ; <i>S. typhi</i> ; <i>S. aureus</i>
<i>Allium sativum</i> (Liliaceae)	<i>B. subtilis</i> ; <i>S. aureus</i> ; <i>S. mutans</i> <i>B. subtilis</i> ; *** H-17(rec+); <i>C. perfringens</i> ; <i>E. amylovora</i> ; <i>E. coli</i> ; <i>K. pneumoniae</i> ; <i>X. campestris</i> ; <i>P. aeruginosa</i> ; <i>S. enteritidis</i> ; <i>S. aureus</i> ; <i>S. sanguis</i> ; <i>E. carotovora</i>
<i>Aloe vera</i> {Liliaceae}	
<i>Citrus reticulata</i> {Rutaceae}	
<i>Oenothera biennis</i> {Onagraceae}	<i>B. subtilis</i> ; <i>C. xerosis</i> ; <i>P. vulgaris</i>
<i>Plantago major</i> {Plantaginaceae}	<i>E. coli</i> ; <i>P. vulgaris</i> ; <i>P. aeruginosa</i> ; <i>S. mutans</i>

Phytochemical	Known Target Organism
<i>Punica granatum</i> {Punicaceae}	<i>S. mutans</i>
<i>Ribes nigrum</i> {Saxifragaceae}	<i>S. dysenteriae</i>
<i>Camellia sinensis</i> {Theaceae}	<i>B. anthracis</i> ; <i>B. subtilis</i> ; <i>E. coli</i> ; *** <i>K. pneumoniae</i> ; <i>P.</i>
<i>Curcuma longa</i> {Zingiberaceae}	<i>aeruginosa</i> ; <i>S. aureus</i>
<i>Zingiber officinale</i> {Zingiberaceae}	<i>E. coli</i>
	<i>Actinomycete sp.</i> ; <i>B. pertussis</i> ; <i>E. coli</i> ; <i>P. shigelloides</i> ; <i>P.</i>
	<i>aeruginosa</i> ; <i>S. aureus</i> ; <i>V. cholera</i>
	<i>B. subtilis</i> ; <i>L. acidophilus</i> ; <i>H-17(rec+)</i>
	<i>B. subtilis</i> ; <i>B. anthracis</i> ; <i>E. coli</i> ; <i>L. acidophilus</i> ; <i>S. aureus</i>
Anti-fungal	
<i>Annona muricata</i> {Annonaceae}	<i>Penicillium oxalicum</i>
<i>Panax ginseng</i> {Araliaceae}	<i>Rhizopus nigricans</i> ; <i>Saccharomyces uvarum</i>
<i>Capparis spinosa</i> (Capparidaceae)	<i>Candida pseudotropicalis</i>
<i>Calendula officinalis</i> (Compositae)	<i>Neurospora crassa</i> ; <i>Candida albicans</i> ; <i>C. monosa</i>
<i>Cucurbita pepo</i> (Cucurbitaceae)	<i>Neurospora crassa</i>
<i>Cymbopogon citratus</i> (Gramineae)	<i>Absidia spinosa</i> ; <i>Alternaria solani</i> ; <i>Aspergillus niger</i> ;
	<i>Curvularia lunata</i> ; <i>Epidermophyton floccosum</i> ;
	<i>Microsporum audouinii</i> ; <i>Trichophyton mentagrophytes</i> ;
<i>Mentha spicata</i> (Labiatae)	<i>Candida albicans</i> ; <i>Cryptococcus neoformans</i> ;
<i>Ocimum basilicum</i> (Labiatae)	<i>Saccharomyces cerevisiae</i>
	<i>A. niger</i> ; <i>F. oxysporum</i> ; <i>F. sp. Lentis</i> ; *** <i>Trichophyton</i>
<i>Rosmarinus officinalis</i> (Labiatae)	<i>rubrum</i>
<i>Glycyrrhiza glabra</i>	<i>Absidia ramosa</i> ; *** <i>Alternaria longipes</i> ; <i>Aspergillus</i>
(Leguminosae)	<i>aegyptiacus</i> ; <i>A. awamori</i> ; <i>Microsporum gypseum</i> ;
<i>Allium sativum</i> (Liliaceae)	<i>Trichoconiella padwickii</i> ; <i>C. albicans</i> ; <i>Kloeckera</i>
	<i>apiculata</i>
	<i>F. oxysporum</i> ; <i>M. icrosporum canis</i> ; <i>P. cyclopium</i> ; <i>C.</i>
	<i>albicans</i> ; <i>Rhodotorula rubra</i> ; <i>T. rubrum</i>
<i>Aloe vera</i> (Liliaceae)	<i>Aspergillus auricomus</i> ; <i>T. mentagrophytes</i> ; <i>C. albicans</i>
<i>Sesamum indicum</i> {Pedaliaceae}	<i>A. aegyptiacus</i> ; *** <i>A. fumigatus</i> ; <i>A. niger</i> ; <i>Botryotrichum</i>
<i>Punica granatum</i> {Punicaceae}	<i>keratinophilum</i> ; <i>E. floccosum</i> ; <i>F. moniliforme</i> ; <i>F.</i>
<i>Citrus aurantium</i> {Rutaceae}	<i>oxysporum</i> ; <i>Geotrichum candidum</i> ; <i>M. canis</i> ; <i>Nannizzia</i>
<i>Citrus reticulata</i> {Rutaceae}	<i>fulva</i> ; <i>Penicillium digitatum</i> ; <i>T. rubrum</i> ; <i>T. semii</i> ; <i>C.</i>

Phytochemical	Known Target Organism
<i>Ribes nigrum</i> {Saxifragaceae}	<i>albicans</i> ; <i>C. krusei</i> ; <i>C. pseudotropicalis</i> ; <i>C. neoformans</i> ;
<i>Camellia sinensis</i> {Theaceae}	<i>Debaryomyces hansenii</i> ; <i>Kloeckera apiculata</i> ; <i>Rhizopus</i>
<i>Curcuma longa</i> {Zingiberaceae}	<i>rhizopodiformis</i> ; <i>T. padwickii</i>
<i>Zingiber officinale</i> {Zingiberaceae}	<i>T. Mentagrophytes</i>
	<i>Cladosporium cucumerinum</i>
	<i>A. niger</i> ; <i>C. albicans</i> ***
	<i>A. aegyptiacus</i> ;*** <i>T. rubrum</i> ; <i>C. albicans</i> ; <i>C. lipolytica</i>
	<i>A. niger</i> ; <i>P. cyclopium</i> ; <i>C. albicans</i>
	<i>P. digitatum</i>
	<i>E. floccosum</i> ; <i>T. mentagrophytes</i> ; <i>S. cerevisiae</i> ;
	<i>Alternaria tenuis</i>
	<i>Debaryomyces hansenii</i> ; <i>A. flavus</i> ; <i>A. niger</i> ; <i>E.</i>
	<i>floccosum</i> ; <i>Trichoderma viride</i>
	<i>A.niger</i> ; <i>A. auricomus</i> ; <i>A. flavus</i> ; <i>Botrytis cinerea</i> ; <i>N.</i>
	<i>crassa</i> ; <i>T. padwickii</i> ; <i>C. albicans</i> ; <i>S. pastorianus</i>
Anti-viral	
<i>Annona squamosa</i> (Annonaceae)	<i>HIV-1</i>
<i>Panax ginseng</i> {Araliaceae}	<i>Adenovirus 3</i> ; <i>herpes simplex 1 virus</i> ; <i>semlicki-forest</i>
<i>Capparis spinosa</i> (Capparidaceae)	<i>virus</i> ; <i>rauscher murine leukemia virus</i>
<i>Calendula officinalis</i> (Compositae)	<i>Hepatitis virus</i>
<i>Mentha spicata</i> (Labiatae)	<i>Encephalitis virus-unspec.</i> ; <i>herpes simplex virus</i> ; <i>HIV-1</i>
<i>Rosmarinus officinalis</i> (Labiatae)	<i>Herpes virus type 2</i>
<i>Glycyrrhiza glabra</i> (Leguminoseae)	<i>Herpes virus type 2</i>
<i>Allium sativum</i> {Liliaceae}	<i>Rauscher murine leukemia virus</i>
<i>Aloe vera</i> {Liliaceae}	<i>Cytomegalovirus</i> ; <i>herpes simplex 1 virus</i> ; <i>herpes simplex</i>
<i>Punica granatum</i> {Punicaceae}	<i>2 virus</i>
<i>Ribes nigrum</i> {Saxifragaceae}	<i>Cytomegalovirus</i> ; <i>herpes simplex 1 virus</i>
<i>Camellia sinensis</i> {Theaceae}	<i>Coxsackie B5 virus</i> ; <i>hepatitis B virus</i> ; <i>herpes simplex 1</i>
<i>Curcuma longa</i> {Zingiberaceae}	<i>virus</i> ;*** <i>herpes simplex 2 virus</i>
<i>Zingiber officinale</i> {Zingiberaceae}	<i>Encephalitis virus (tick-borne)</i>
	<i>Coxsackie A9 virus</i> ; <i>influenza virus A</i> ; <i>influenza virus A2</i>
	<i>(manheim 57)</i> ; <i>poliovirus I</i>

Phytochemical	Known Target Organism
	<i>Hepatitis B virus</i> ; <i>vesicular stomatitis virus</i> <i>Herpes simplex 1 virus</i> ; <i>rhinovirus type 1-B</i> ; <i>virus-lpp1</i> ; <i>rauscher murine leukemia virus</i>
Anti-crustacean	
<i>Annona muricata</i> (Annonaceae)	<i>Artemia salina</i> larvae; <i>Artemia salina</i> ***
<i>Zingiber officinale</i> (Zingiberaceae)	<i>Artemia salina</i>
Insecticide	
<i>Annona muricata</i> (Annonaceae)	<i>Macrosiphoniella sanborni</i> ***
<i>Annona reticulata</i> (Annonaceae)	<i>Macrosiphoniella sanborni</i> ;*** <i>Oryzaephilus</i>
<i>Annona squamosa</i> (Annonaceae)	<i>surinamensis</i> ; <i>Tribolium castaneum</i> <i>Callosobruchus chinensis</i> ; <i>Drosophila melanogaster</i> ;
<i>Cucurbita pepo</i> (Cucurbitaceae)	<i>M.Sanborni</i> ;*** <i>Musca Domestica</i> ; <i>Pediculus Capitis</i>
<i>Mammea americana</i> (Guttiferae)	<i>Culex quinquefasciatus</i>
<i>Mentha spicata</i> (Labiatae)	<i>Aedes aegypti</i> ;*** <i>Serotoma ruficornis</i> ,adults***
<i>Ocimum basilicum</i> (Labiatae)	<i>Drosophila auraria</i> ; <i>Mites (Pyroglyphidae)</i>
<i>Rosmarinus officinalis</i> (Labiatae)	<i>Culex quinquefasciatus</i>
<i>Citrus reticulata</i> (Rutaceae)	<i>Drosophila auraria</i>
<i>Curcuma longa</i> (Zingiberaceae)	<i>Sitophilus granarius</i> <i>Macrosiphum euphorbiae</i>
Larvicidal	
<i>Annona squamosa</i>	<i>Anopheles stephensi</i> larvae
<i>Mammea americana</i> (Guttiferae)	<i>Diaphania hyalinata</i> ; <i>Laphygma frugiperda</i> ***
<i>Ocimum Basilicum</i> (Labiatae)	<i>Culex fatigans</i> ;*** <i>Diacrisia obliqua</i>
<i>Allium sativum</i> (Liliaceae)	<i>Culex pipiens-quinquefasciatus</i> (1st instar larvae)
<i>Curcuma longa</i> (Zingiberaceae)	<i>Spodoptera litura</i> Larvae
Molluscicidal	
<i>Annona squamosa</i> (Annonaceae)	
<i>Ocimum Basilicum</i> (Labiatae)	<i>Biomphalaria straminea</i>
<i>Camellia sinensis</i> (Theaceae)	<i>Biomphalaria pfeifferi</i> <i>Biomphalaria glabrata</i>
Antinematodal	

Phytochemical	Known Target Organism
<i>Glycyrrhiza glabra</i> (Leguminosae)	<i>Meloidogyne Incognita</i> ***
<i>Phaseolus vulgaris</i> (Leguminosae)	<i>Heterodera glycines</i>

***strong activity for phytochemical

One aspect of the present invention, therefore, provides paint and coating compositions, especially a marine paint for the anti-fouling treatment of the submerged portion of the hull of a ship or boat, water intake and discharge systems for reservoirs and nuclear power plants, comprising an environmentally friendly anti-fouling additive in the form of at least one phytochemical and menthol. In general terms, the present invention is directed to paints, coatings and polymers containing phytochemicals and methods of making and using the same. Phytochemicals especially useful in the present invention include, but are not limited to, grapefruit seed extract, capsicum preparations, tannins, tannic acid, neem oil, menthol, camphor, camphor oil, zosteric acid, *Zostera noltii* (eel grass), eel grass extract, lemon grass oil, myrtle oil, thyme extract, rosemary, sage, bayleaf, oregano, tea tree oil, clove oil, garlic, citric acid, vitamin E, and other phytochemicals exhibiting activity to be used in any combination or derivatives thereof wherein the derivative may be active alone or in combination with a natural phytochemical or biocide to inhibit the colonization of a treated surface. Grapefruit seed extract is an effective phytochemical biocide with activity against bacteria, fungi, algae and some parasites and is available commercially as CITRICIDAL from Bio/Chem Research (Lakeport, CA). Capsicum preparations that may be used in the invention may be, but not necessarily so, substantially free of capsaicin, the pungency component of the 'hot pepper extracts'. Capsicum is available commercially from, for example Kalsec, Inc., Kalamazoo, MI. Menthol, tea tree oil, clove oil, citric acid, garlic extract, thyme extract are commercially available from Aldrich Chemical, Los Angeles, CA. Menthol derivatives, such as FRESCALINTM, suitable for use in the present invention are commercially available from Symrise, GmbH & Co., Holzminden, Germany.

The rate of migration or the release of the phytochemical composition contained within the marine and architectural paints, coatings and polymers may be modified by further including in the compositions a release agent such as Vitamin E, a chemical releaser such as citric acid, or an anti-oxidant such as Vitamin E. The chemical releaser may be the same as the phytochemical agent. Vitamin E further possesses antimicrobial properties, and thus may function as a phytochemical, which may work in conjunction with or separately from marine paint binders.

Phytochemicals suitable for use in the compositions of the present invention and which are known to function as anti-oxidants, as well as to possess antimicrobial properties include, but are not limited to, *Panax ginseng*; *Panax quinquefolius*; *Bixa orellana*; *Humulus lupulus*; *Spinacia oleracea*; *Arctium lappa*; *Cichorium intybus*; *Cynara scolymus*;
 5 *Helianthus annuus*; *Inula helenium*; *Armoracia rusticana*; *Momordica charantia*; *Vaccinium corymbosum*; *Vaccinium myrtillus*; *Avena sativa*; *Oryza sativa*; *Lavandula latifolia*; *Marrubium vulgare*; *Melissa officinalis*; *Mentha pulegium*; *Mentha spicata*; *Nepeta cataria*; *Ocimum basilicum*; *Origanum onites*; *Perilla frutescens*; *Prunella vulgaris*; *Rosmarinus officinalis*; *Salvia officinalis*; *Salvia sclarea*; *Satureja hortensis*; *Thymus vulgaris*; *Laurus*
 10 *nobilis*; *Arachis hypogaea*; *Glycine max*; *Glycyrrhiza glabra*; *Glycyrrhiza uralensis*; *Lens culinaris*; *Phaseolus coccineus*; *Phaseolus lunatus*; *Phaseolus vulgaris*; *Phaseolus vulgaris*; *Pisum sativum*; *Psophocarpus tetragonolobus*; *Pueraria lobata*; *Tamarindus indica*; *Tamarindus indica*;* *Vicia faba*; *Vigna angularis*; *Vigna mungo*; *Vigna radiata*; *Allium ampeloprasum*; *Allium cepa*; *Allium sativum*; *Asparagus officinalis*; *Linum usitatissimum*;
 15 *Morus alba*; *Eucalyptus globulus*; *Pimenta dioica*; *Syzygium aromaticum*; *Olea europaea*; *Oenothera biennis*; *Sesamum indicum*; *Plantago asiatica*; *Fagopyrum esculentum*; *Prunus cerasus*; *Prunus spinosa*; *Rosa canina*; *Rubus fruticosus*; *Rubus idaeus*; *Coffea arabica*; *Citrus aurantium*; *Citrus paradisi*; *Ribes nigrum*; *Ribes rubrum*; *Capsicum frutescens*; *Solanum tuberosum*; *Solanum tuberosum*;* *Theobroma cacao*; *Camellia sinensis*;
 20 *Coriandrum sativum*; *Cuminum cyminum*; *Daucus carota*; *Trachyspermum ammi*; *Vitis vinifera*; *Curcuma longa*; *Zingiber officinale*. Other antioxidants that are useful in the present invention include, but are not limited to, lysine, butylatedhydroxytoluene (BHT), butylatedhydroxyanisole (BHA), grape seed extract, Pine Bark extract (Proanthocyanidins), β -carotene, bilberry extract, ascorbic acid, *Ginkgo biloba* extract, green tea extract, tumeric,
 25 zinc picolinate, zinc oxide, iron oxide, calcium carbonate and selenium. Selected antioxidant(s) may be used alone or in combination when combined with the phytochemical(s) in the coating formulas of the present invention.

For applications using leaching paints (coatings), ablative paints (coatings) or self-polishing coatings (polymers) wherein the phytochemical component of the paint
 30 compositions comprises a capsicum preparation, grapefruit seed extract, menthol, thyme, clove oil, rosemary, sage, bayleaf, oregano, lemon grass oil tannin, tannic acid, camphor, camphor oil or *Zostera noltii*, (eel grass extract or derivatives thereof) for their organism inhibiting activity, with or without a migration release agent, the components of the leaching

paints (coatings), ablative paints (coatings) and self-polishing polymers (coatings) may contain any combination of the primers, resins, pigments, solvents, paint binders and anti-settling agents known to those of skill in the art that provide effective application properties to, for example, the submerged region of a ship's hull

5 It should be understood that the present invention is broadly drafted, in one embodiment, towards incorporating a phytochemical or combination of phytochemicals into polymeric materials as agents to inhibit the colonization of a painted surface by animal and/or plant organisms. In several preferred embodiments of the present invention, capsicum, menthol and grapefruit seed extract may be used as agents. The present invention, however,
10 encompasses the use of many other agents. In the various embodiments of the invention, a preferred phytochemical is a capsicum preparation, alone or in combination with other phytochemicals for use as a fouling preventive agent in marine paints (coatings). Capsicum is a food or food seasoning commonly known as "hot pepper." The active heat ingredient in capsicum is capsaicin which is a mixture of two unsaturated and three saturated homologs.
15 This mixture is also referred to as capsaicinoids, and includes dihydrocapsaicin and nordihydrocapsaicin. The pungency of capsaicin (capsaicinoids) is measured in Scoville heat units and typically ranges from 60,000 to 1,500,000 heat units. The compositions of the present invention, however, may comprise capsicum preparations having Scoville heat units from about 0 to at least 1.5 million. While capsaicin itself does not have antimicrobial
20 qualities, other chemical ingredients in capsicum do have antimicrobial activity, such as; 1,8-cineole, acetic acid, alpha-terpineol, benzaldehyde, beta-ionone, caffeic acid, caryophyllene, chlorogenic acid, cinnamic acid, delta-3-carene, ferulic-acid, limonene, myrcene, p-coumaric-acid, pulegone, quercetin, rutin, scopoletin, terpinen-4-ol and thujone. It is contemplated, therefore, that a capsicum preparation with the removal of the active heat
25 ingredients, either partially or totally, for use as an anti-fouling additive in marine and especially in architectural paints (coatings), is possible, even though the heat unit index, before processing of the capsicum may have been at any value, it would no longer have a pungency factor in the finished product.

 Also useful in the present invention as a fouling preventive additive in marine paints
30 (coatings) is the phytochemical tannic acid. Tannins are classified into two broad groups: the hydrolysable and the condensed or non-hydrolysable tannins. The hydrolysable tannins are usually compounds containing a central core of glucose or other polyhydric alcohol esterified with gallic acid (gallotannins) or hexahydroxydiphenic acid (ellagitannins). The condensed ones are mostly flavolans or polymers of flavan-3-ols (catechins) and/or flavan 3:4-idols

(leucoanthocyanidins). They are more resistant to breakdown. Frequently, tannins isolated from a plant bear the characteristics of both groups. Tannins may occur in almost any part of a plant-root, stem, trunk bark, leaves and fruit.

5 Neem (*Azadirachta indica*). repels and disrupts the growth and reproduction of destructive insect species. Low doses of azadirachtin, an active anti-insect component of neem and extracts thereof, have little or no mammalian toxicity. Insects affected by neem include termites, beetles, flies, caterpillars, true bugs, aphids, weevils, and roaches. Components of neem extracts comprise about 50% oleic acid, about 20% stearic acid, about 12.6% palmitic acid, about 2% linoleic acid and about 2% lower fatty acids.

10 The compositions of the invention may further comprise menthol or a derivative thereof such as, but not limited to, mentholpropylreneglycolcarbonate. A particularly useful synthetic menthol preparation for inclusion in the compositions of the present invention is FRESCALINTM (Symrise GmbH & Co, Holzminden, Germany) and comprising at least 50% by weight of isopulegol, between .01% and 49.99% by weight of 5-methyl-2-(1-methylethyl)-
15 cyclohexanol and between .01% and 49.99% by weight of mentholpropylreneglycolcarbonate. This synthetic menthol preparation is especially effective with any combination of capsicum, grapefruit seed extract or natural menthol at inhibiting marine growth when included in anti-fouling paints and coatings.

20 The compositions of the present invention may further include a chemical releaser, which is used to facilitate the controlled release of the phytochemical from the polymer or paint matrix. The chemical releaser facilitates the release of the phytochemical composition from the polymer or paint. The releaser may be, for example, citric acid, a phytochemical that also exhibits antibacterial activity. Zinc oxide, iron oxide or citric acid extract can be added to the polymer or paint (coatings) alone or in combination with other phytochemicals,
25 with or without anti-oxidants like Vitamin E. The release agents used in the phytochemicals and the release agents used in the marine paints, coatings and polymers can have a synergistic effect, depending on the desired release, erosion or ablative rate of the marine paints, coatings and polymers containing phytochemicals to prevent marine organism fouling.

30 While not wishing to be bound by any one theory, the addition of the phytochemicals to the paint base increase the efficacy of the applied paint to remove newly attached organisms by slowing or inhibiting the attachment and growth of the animals and plants. This delay in their forming a firm attachment such as, for example, through the development of a secure holdfast by algae allows the ablative loss of the outer surface of the paint layer to more effectively dislodge the organisms. In the case of architectural paints applied to a non-

submerged surface, the reduction in the colony load can allow more effective removal of the outer paint layer and any cells clinging thereto. It is also contemplated, however, that the phytochemicals can be effective in repelling non-attaching organisms such as termites that may otherwise penetrate or contact a painted layer.

5 The amounts (by volume or by weight) and combinations (number) of the phytochemical agents added to the paints (coatings) therefore may be adjusted according to the particular application, relevant factors including the conditions under which the phytochemical composition is to be used, the type of paint, coating or polymer (leaching, ablative, self-polishing), the thickness of the paint, coating or polymer, the rate of release of
10 the phytochemical and the leach, ablation or polishing rate, the types of marine organisms that need controlling may vary, the duration of the use of the phytochemicals in these coatings, and the active concentration of the phytochemical desired. In some cases there may be a need for additional substances such as wetting or emulsifying agents, pH buffering agents, adjuvants, gelling or viscosity enhancing additives, preservatives, colors, and the like,
15 depending upon the use. The present invention also provides paint compositions, and their methods of use, formulated for application in non-marine environments such as architectural paints. In such cases, the rate of leaching of the agents will not be as great as if the paint is immersed in marine or freshwater, and the effective amount of the phytochemicals can be adjusted accordingly. In the case of architectural paint formulas that incorporate
20 phytochemicals, oxidizers may be used to cause oxidation and loss of the paint surface in a manner similar to that of zinc oxide which enhances the ablation of the paint surface in an aqueous environment.

When making any of the compositions of the present invention, the phytochemicals, menthol and other desired components may be added either together or sequentially to a paint
25 base selected for the particular application. The mixture is then mixed until the phytochemicals are evenly dispersed within the paint, coating or polymer. The applications of the finished product may be brushed or sprayed on a surface to be coated.

In various embodiments of the paints and coatings of the present invention, phytochemicals of the present invention may be added in any combination to leaching paints
30 (hard and soft), ablative paints (coatings), self-polishing coatings (polymers), long life anti-fouling coatings and fouling-release coatings at levels of at least .01% to about 60% by v/v or weight to weight of the paint base.

In one embodiment of the present invention, the phytochemicals can be active in the inhibition or control of hard marine fouling (e.g. barnacles) and soft fouling (for example by

algae) or a phytochemical may only be active against one type of fouling, and therefore a combination of phytochemicals is required to achieve efficacy. In various embodiments of the invention, the phytochemical capsicum is combined with one or more other phytochemicals and added to a marine paint or coating to control marine fouling.

5 In other embodiments of the invention, the phytochemical capsicum is combined with one or more other phytochemicals and added to an architectural paint or coating to control biological colonization (fungal, algal or bacterial attachment) of an architectural painted surface. In one embodiment, the phytochemical, capsicum may be combined with other phytochemicals and added to marine paint to control marine fouling, wherein the capsicum is
10 substantially free of the heat causing ingredient capsaicin.

The phytochemical grapefruit seed extract may be added to paint (coatings) to control marine fouling. In one embodiment of the invention, the phytochemical grapefruit seed extract may be processed into a concentrated state and the glycol substantially removed from the extract before adding to marine paint or coating. In another embodiment, the
15 phytochemical may be selected from extracts of cloves, rosemary, sage, bayleaf, oregano, eel grass, thyme, garlic and/or clove oil. In preferred embodiments of the invention, the paint comprises a paint base, grapefruit seed extract, a menthol or a preparation such as FRESCALINTM that comprises a menthol derivative, and a capsicum preparation.

The phytochemical grapefruit seed extract exhibits anti-bacterial, anti-parasitic and
20 anti-fungal activity. Grapefruit seed extract is available commercially such as CITRICIDALTM. The grapefruit seed extract can be added to architectural and marine paints alone or in combination with other phytochemicals, or in combination with antioxidants such as Vitamin E or oxidizers or photosensitive compounds suitable for chemically disrupting the outer surface of the applied paint.

25 In an alternative embodiment, the phytochemical camphor is used in combination with other phytochemicals as a marine organism-fouling preventive. Camphor is a crystalline ketone derived from the wood of the camphor tree *Cinnamomum camphora*. In another alternative embodiment, the paint phytochemical additive for fouling prevention may be lemon grass oil which is a natural by-product of lemon grass and is extracted by steam and
30 other nontoxic extraction methods. Lemon grass oil exhibits anti-fungal and anti-bacterial activity and may be added to marine paints in combination with other phytochemicals. Antioxidants, such as Vitamin E, or releasers, such as citric acid may also be added with the phytochemical composition to the marine paints.

In yet another alternative embodiment, the paint-fouling preventive may be Tea Tree oil. Tea Tree Oil is a natural by-product of the tea tree, (*Melaleuca* species). Tea Tree Oil is extracted through natural non-toxic processes such as steam. Tea Tree Oil exhibits anti-fungal and anti-bacterial activity. Tea Tree Oil may be added to marine paints in combination with other phytochemicals, oxidizing releasers, or antioxidants like Vitamin E.

In other embodiments of the compositions of the present invention, the phytochemical component may be selected from neem oil, tannic acid (tannins), menthol or derivatives thereof, camphor oil, clove and/or clove oil and garlic. In one embodiment of the compositions of the present invention, the phytochemical combination comprises a capsicum preparation and tannic acid, and menthol or a derivative thereof. In another embodiment, the phytochemical combination comprises capsicum, tannic acid, clove oil, garlic and menthol. In yet another embodiment the phytochemical combination comprises a capsicum preparation, tannic acid, garlic and clove oil.

In one embodiment of the paints and coatings of the present invention, the phytochemical combination comprises capsicum and clove oil and optionally garlic. In another embodiment the phytochemical combination comprises capsicum, clove oil, garlic and *Zostera noltii* (eel grass), with or without vitamin E. In one embodiment the phytochemical combination comprises capsicum, tannic acid, menthol and *Zostera noltii* (eel grass). In still another embodiment the phytochemical combination comprises a capsicum preparation, menthol, grapefruit seed extract and *Zostera noltii* (eel grass). In still another embodiment of the invention, the phytochemical combination comprises a capsicum preparation, menthol, grapefruit seed extract, neem oil and *Zostera noltii* (eel grass). In yet another embodiment, the phytochemical combination comprises a capsicum preparation, menthol, and neem oil.

In embodiments of the paints and coatings of the present invention, phytochemicals of the present invention may be added in any combination to leaching paints (hard and soft), ablative paints (coatings), self-polishing coatings (polymers), longlife anti-fouling coatings and fouling-release coatings, at levels from about .01% to about 60% by volume or weight to weight. In other embodiments of the paints and coatings of the present invention, phytochemicals of the present invention may be added in any combination to leaching paints (hard and soft), ablative paints (coatings), self-polishing coatings (polymers), longlife anti-fouling coatings and fouling-release coatings, at levels from about .01% to about 50% by volume or weight to weight.

A concentrate (liquid or powder) comprising about 4% capsicum may be used in the paint compositions of the invention at a concentration of between about .01% and about 60% v/v or weight to weight of a liquid paint base. In one embodiment of the compositions of the invention, the 4% capsicum concentrate (liquid or powder) may be between about .01% to
5 about 15% v/v or weight to weight of a liquid paint base. In another embodiment, a concentrate (liquid or powder) comprising about 14% capsicum may be used at a concentration of between about .01% to about 60% v/v or weight to weight of a liquid paint base, preferably between about .01% to about 15% v/v or weight to weight of a liquid paint base. In yet another embodiment, a concentrate (liquid or powder) comprising about 87%
10 capsicum may be used at a concentration of between about .01% to about 60% v/v or weight to weight of a liquid paint base, preferably between about .01% to about 15% v/v or weight to weight of a liquid paint base. In the various embodiments of the invention, menthol (liquid, crystals or powder) may be included at a concentration of between about .01% and about 60% v/v or weight to weight of a liquid paint base. In other embodiments, the concentration
15 of the menthol may be between about .01% to about 15% v/v or weight to weight of the liquid paint base.

In another embodiment of the invention, the compositions may further comprise a mixture, said mixture comprising grapefruit seed extract and menthol (liquid, crystals or powder) in a weight-to-weight ratio range of from about 0.5:1 to about 2:1, the final
20 concentration of the mixture in the paint composition being between about .01% to about 60% v/v or weight to weight of a liquid paint base. In further embodiments, the final concentration of the grapefruit seed extract and menthol mixture comprises between about .01% to about 25% v/v or weight to weight of a liquid paint base. In other compositions of the invention, the mixture added to the paint base is between about .01% to about 25% v/v or
25 weight to weight of a liquid paint base

Another embodiment of the invention comprises a paint base with FRESCALINTM at between about .01% and about 60% (liquid or powder) of a liquid paint base, and about 4% capsicum at a concentration of between about .01% to about 60% v/v or weight to weight of a liquid paint base. In one embodiment of the invention wherein the compositions comprise
30 FRESCALINTM at between about .01% and about 15% v/v or weight to weight, the 4% capsicum concentrate (liquid or powder) may be between about .01% to about 15% v/v or weight to weight of a liquid paint base. In another embodiment, a concentrate (liquid or powder) comprising about 14% capsicum may be used at a concentration of between about .01% to about 60% v/v or weight to weight of a liquid paint base, preferably between about

.01% to about 15% v/v or weight to weight of a liquid paint base. In yet another embodiment, a concentrate (liquid or powder) comprising about 87% capsaicin may be used at a concentration of between about .01% to about 60% v/v or weight to weight of a liquid paint base, preferably between about .01% to about 15% v/v or weight to weight of a liquid paint base.

In the various embodiments of the paints and coatings of the present invention, phytochemicals may be added in any combination to any type of leaching paints (coatings) (hard and soft), ablative paints (coatings), self-polishing coatings (polymers), the ablative and self-polishing paints further comprising a primer, a resin, a pigment, a solvent, a paint binder and an anti-settling agent

It should be understood that the present invention is not limited to the specific compositions or methods described herein and that any composition having a formula or method steps equivalent to those described falls within the scope of the present invention. Preparation routes of the composition and method steps for treating marine surfaces are merely exemplary so as to enable one of ordinary skill in the art to make the composition and use it according to the described process and its equivalents. It will also be understood that although the form of the invention shown and described herein constitutes preferred embodiments of the invention, it is not intended to illustrate all possible forms of the invention. The words used are words of description rather than of limitation. Various changes and variations may be made to the present invention without departing from the spirit and scope of the invention.

Example 1: Anti-fouling of marine immersed painted surfaces

A marine paint composition having the formula of .7% by volume of a 14% capsaicin preparation and .4% by weight of menthol was used to coat the surface of a metal plate. Control plates were similarly coated with a paint not containing the agents, or with a commercially available marine anti-fouling paint. The plates were immersed in open ocean water and periodically examined for the extent of marine colonization.

At the end of six months of immersion, the control metal plates were heavily encrusted with both animal and plant growth including brown and green algae, acorn barnacles and marine worms. In contrast, however, the plates treated with the paint comprising the .7% by volume of a 14% capsaicin preparation and .4% by weight of menthol had very little marine growth over more than 90% of the exposed surface, and where there was growth it was significantly less than would be expected for the period of exposure used.

What is claimed is

1. A paint composition for application to a surface for inhibiting the colonization of a painted surface by organisms, the paint composition comprising:
a paint base selected from a marine paint base and an architectural paint base, and
5 wherein the paint base is selected from an epoxy based paint, a silicone based paint, a polyurea resin, an alkyl, a polyvinyl acetate emulsion, a polyvinyl chloride emulsion, a water based epoxy resin, an acrylic emulsion, an acrylic resin, a copolymer, a synthetic composite, a vinyl, an ablative paint, a self-polishing paint, a leaching paint, a non-leaching paint, an oil-based paint, an aqueous-based paint and derivatives thereof;
10 a phytochemical dispersed within the paint base, the phytochemical being present in the paint base in an amount sufficient to inhibit the colonization of the painted surface by organisms that come into contact with a surface coated with the paint composition.
2. The paint composition according to claim 1, wherein the phytochemical is selected from a
15 capsicum preparation, menthol, a menthol derivative, grapefruit seed extract, lemon grass oil, rosemary, sage, bayleaf, oregano, myrtle oil, tea tree oil, citric acid, thyme, *Zostera noltii* (eel grass extract or derivatives thereof), tannin, neem oil or derivatives or mixtures thereof.
3. The paint composition according to claim 1, further comprising a capsicum preparation,
20 wherein the capsicum preparation has between about 4% capsicum and about 90% capsicum and has a concentration in the paint composition of between about .01% to about 60% v/v or weight to weight of a liquid paint base or between about .01% to about 15% v/v or weight to weight of a liquid paint base.
4. The paint composition according to claim 3, wherein the capsicum preparation has about
25 4% capsicum, about 14% capsicum or about 90% capsicum, and wherein the capsicum preparation is optionally is substantially free of capsaicin.
5. The paint composition according to claim 1, wherein the phytochemical is a mixture comprising grapefruit seed extract and menthol in a weight-to-weight ratio range of from about 0.5:1 to about 2:1, the final concentration of the phytochemical mixture in
30 the paint composition being between about .01% to about 60% v/v or weight to weight of a liquid paint base.
6. The paint composition according to claim 5, wherein the final concentrations of the grapefruit seed extract and menthol are each between about .01% to about 25% v/v or weight to weight of a liquid paint base.

7. The paint composition according to claim 5, wherein the menthol or the menthol derivative each has a concentration in the paint composition of between about .01% and about 60% v/v or weight to weight of a liquid paint base.
8. A paint composition for application to a surface for inhibiting the colonization of a painted surface by organisms, the paint composition comprising:
5 a paint base selected from the group consisting of an epoxy based paint, a silicone based paint, a polyurea resin, an alkyl, a polyvinyl acetate emulsion, a polyvinyl chloride emulsion, a water based epoxy resin, an acrylic emulsion, an acrylic resin, a copolymer, a synthetic composite, a vinyl, an ablative paint, a self-polishing paint, a leaching paint, a non-leaching paint, an oil-based paint, an aqueous-based paint;
10 at least one phytochemical dispersed within the paint base, the phytochemical being present in the paint base in an amount sufficient to inhibit the colonization of the painted surface by organisms that come into contact with a surface coated with the paint composition, wherein the phytochemical is selected from the group consisting of
15 a capsicum preparation, grapefruit seed extract, lemon grass oil, myrtle oil, tea tree oil, neem oil, citric acid, thyme, rosemary, sage, bayleaf, oregano, eel grass extract, tannin or mixtures thereof; and
a menthol or a menthol derivative.
9. A paint composition for application to a surface for inhibiting the colonization of a painted surface by organisms, the paint composition comprising:
20 a paint base selected from the group consisting of an epoxy based paint, a silicone based paint, a polyurea resin, an alkyl, a polyvinyl acetate emulsion, a polyvinyl chloride emulsion, a water based epoxy resin, an acrylic emulsion, an acrylic resin, a copolymer, a synthetic composite, a vinyl, an ablative paint, a self-polishing paint, a leaching paint, a non-leaching paint, an oil-based paint, an aqueous-based paint;
25 at least one phytochemical dispersed within the paint base, the phytochemical(s) being present in the paint base in an amount sufficient to inhibit the colonization of the painted surface by organisms that come into contact with a surface coated with the paint composition, wherein the phytochemical(s) is selected from the group consisting of
30 of grapefruit seed extract, lemon grass oil, myrtle oil, neem oil, tea tree oil, citric acid, thyme, rosemary, sage, bayleaf, oregano, *Zostera Noltii*, eel grass extract or derivative thereof), tannin or mixtures thereof;
a capsicum preparation; and
a menthol or a menthol derivative.

10. A method for treating a surface to discourage the colonization of the surface by organisms, comprising the steps of:

5 mixing from about .01% to about 60% by weight of a selected paint base selected from the group consisting of an epoxy based paint, a silicone based paint, a polyurea resin, an alkyl, a polyvinyl acetate emulsion, a polyvinyl chloride emulsion, a water
10 based epoxy resin, an acrylic emulsion, an acrylic resin, a copolymer, a synthetic composite, a vinyl, an ablative paint, a self-polishing paint, a leaching paint, a non-leaching paint, an oil-based paint and an aqueous-based paint with at least one phytochemical selected from the group consisting of menthol or a menthol derivative, grapefruit seed extract, lemon grass oil, myrtle oil, rosemary, sage, bayleaf, oregano,
15 tea tree oil, citric acid, thyme, eel grass extract, tannin, neem oil or derivatives or mixtures thereof, and optionally a capsicum preparation; and

applying the mixture to a surface to be protected from colonization, whereby the painted surface is resistant to colonization by a plant or animal.

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