

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(10) International Publication Number

WO 2014/074376 A1

(43) International Publication Date

15 May 2014 (15.05.2014)

(51) International Patent Classification:

C09D 5/16 (2006.01)

(21) International Application Number:

PCT/US2013/067647

(22) International Filing Date:

31 October 2013 (31.10.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/722,948 6 November 2012 (06.11.2012) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Published:

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



WO 2014/074376 A1

(54) Title: CONTROLLED RELEASE COMPOSITION CONTAINING DCOIT

(57) Abstract: A composition containing 4,5-dichloro-2-n-octylisothiazolin-3-one and an activated carbon having a surface area of at least 700 m²/g.

CONTROLLED RELEASE COMPOSITION CONTAINING DCOIT

This invention relates to a controlled release composition containing 4,5-dichloro-2-n-octylisothiazolin-3-one (DCOIT).

5 Controlled release compositions containing DCOIT are disclosed in U.S. Pat. No. 6,676,954. However, there is a need for controlled release compositions which release DCOIT at a lower rate.

The problem addressed by this invention is to provide an improved controlled release formulation which provides long-term controlled release of DCOIT.

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STATEMENT OF THE INVENTION

The present invention is directed to a composition comprising 4,5-dichloro-2-n-octylisothiazolin-3-one and an activated carbon having a surface area of at least 700 m²/g.

15 DETAILED DESCRIPTION OF THE INVENTION

Unless otherwise specified, temperatures are in degrees centigrade (°C), references to percentages are percentages by weight (wt%) and amounts and ratios of DCOIT are on an active ingredient basis. As used herein, when a collection of particles has D50 of a certain value, then 50 percent of the particles by volume have a diameter less than or equal to that 20 value. For non-spherical particles, the diameter is the largest dimension. A marine coating composition is a coating composition that is capable of forming a dry coating on the surface of a marine object. After formation of the dry coating, the dry coating will adhere to the surface for a usefully long time, even when some or all of the coated surface remains under water for significant amounts of time (i.e., at least one hour per day). Marine objects are 25 those that are put to use in environments in which some or all of the object is under water for significant amounts of time. Examples of marine objects include ships, piers, docks, pilings, fishnets, heat exchangers, dams, and piping structures, such as intake screens. Preferably, the substrate is a marine object.

Seawater is water from a sea or ocean. On average, seawater in the world's oceans 30 has a salinity of about 3.5 wt% and an average density at the ocean surface of 1.025 g/ml. Artificial seawater is a mixture of water with dissolved mineral salts that simulates seawater. An example of artificial seawater is synthetic seawater available from RICCA (ASTM D1141).

Preferably, DCOIT and the activated carbon are present in a marine coating, i.e., a coating on a marine object. Preferably, the DCOIT and activated carbon are added to the liquid marine coating formulation prior to coating on the surface of the marine object. In one preferred embodiment of the invention, DCOIT and activated carbon are added separately to the liquid marine coating composition. In one preferred embodiment of the invention, DCOIT and activated carbon are combined prior to addition to the liquid marine coating composition. DCOIT may be adsorbed on activated carbon by mixing DCOIT, as a melt or as a solution, with the activated carbon. Suitable solvents for the DCOIT are any which dissolve DCOIT, do not destabilize it and do not react with activated carbon. Suitable solvents include alcohols, such as methanol, ethanol and propanol; esters, such as ethyl acetate and butyl acetate; ketones, such as acetone, methyl iso-butyl ketone and methyl iso-amyl ketone; xylenes; mineral spirits; and nitriles, such as acetonitrile. Preferred solvents are (C₁-C₄)alcohols, xylenes and mineral spirits. Preferably, DCOIT is dissolved or slurried in a solvent prior to mixing with activated carbon or the liquid marine coating.

The substrate for a marine coating may be an uncoated surface, e.g., a marine object, or another coating on the surface of the marine object, e.g., an underlayer of primer or paint on the surface. Preferably, the marine coating is an epoxy coating, a self-polishing coating (e.g., a metal acrylate copolymer paint, typically incorporating zinc or copper carboxylate groups, or a silyl acrylate copolymer paint) or a foul-release coating (e.g., silicone paint).

Marine coating compositions comprise a binder and a solvent and optionally other ingredients. The solvent may be an organic solvent or water. Other ingredients may include inorganic pigments, organic pigments or dyes, and natural resins. Water-based coatings may also contain coalescents, dispersants, surface-active agents, rheology modifiers or adhesion promoters. Solvent-based coatings may also include extenders, plasticizers or rheology modifiers. A typical marine coating composition comprises 5 to 30% binders, up to 15% rosins/ modified rosins, 0.5 to 5% plasticizers, 0.1 to 2% antifouling agent, 5 to 60% solvent, up to 65% cuprous oxide, up to 30% pigments (other than cuprous oxide) and up to 15% marine antifouling agents (including DCOIT). Preferably, the marine coating contains at least 0.5 wt% DCOIT, preferably at least 0.8 wt%, preferably at least 1 wt%, preferably at least 1.2 wt%, preferably at least 1.4 wt%, preferably at least 1.6 wt%, preferably at least 1.8 wt%, preferably at least 2 wt%; preferably the marine coating contains no more than 5 wt% DCOIT, preferably no more than 4.5 wt%, preferably no more than 4 wt%, preferably no more than 3.5 wt%, preferably no more than 3 wt%, preferably no more than 2.5 wt%, preferably no more than 2 wt%, preferably no more than 1.8 wt%. Preferably, the marine

coating contains at least 1 wt% activated carbon, preferably at least 1.5 wt%, preferably at least 2 wt%, preferably at least 2.5 wt%, preferably at least 3 wt%, preferably at least 3.5 wt%; preferably the marine coating contains no more than 20 wt% activated carbon, preferably no more than 16 wt%, preferably no more than 14 wt%, preferably no more than 12 wt%, preferably no more than 10 wt%, preferably no more than 8 wt%.

Preferably, the weight ratio of activated carbon to DCOIT is at least 1:1, preferably at least 1.5:1, preferably at least 2:1, preferably at least 2.5:1, preferably at least 3:1; preferably the weight ratio is no greater than 12:1, preferably no greater than 10:1, preferably no greater than 8:1, preferably no greater than 6:1, preferably no greater than 5:1, preferably no greater than 4.5:1. Preferably, the weight ratio of activated carbon to DCOIT in a self-polishing coating is from 1.5:1 to 5:1, preferably 2:1 to 4:1. Preferably, the weight ratio of activated carbon to DCOIT in a foul release coating is from 2:1 to 10:1, preferably from 2:1 to 8:1, preferably from 3:1 to 8:1.

Preferably, the wet film thickness of the marine coating is at least 25 microns, preferably at least 50 microns, preferably at least 100 microns, preferably at least 200 microns; preferably no more than 500 microns, preferably no more than 400 microns, preferably no more than 300 microns. The thickness of the dry film formed upon cure of the wet coating would be expected to be less than the wet thickness by an amount corresponding to the solvent content of the wet coating material. Preferably, the dry (cured) film thickness of the marine coating is at least 20 microns, preferably at least 40 microns, preferably at least 80 microns, preferably at least 160 microns; preferably no more than 400 microns, preferably no more than 320 microns, preferably no more than 240 microns.

Suitable activated carbons include, for example, carbons such as those derived from coal, wood, coconut shells, lignin or animal bones. Activated carbon can be produced by physical or chemical treatment. Physical treatment entails the combination of the following processes: carbonization, pyrolysis of carbon at temperatures in the range 600–900 °C, under anoxic conditions, and exposure of the carbonized carbon with an oxidative atmosphere (carbon dioxide, oxygen, or steam) at temperatures above 250 °C. Chemical activation entails, prior to carbonization, impregnating the raw material with certain chemicals: an acid, strong base, or a salt (e.g., phosphoric acid, potassium hydroxide, sodium hydroxide, calcium chloride, and zinc chloride 25%), followed by carbonizing at lower temperatures (450–900 °C). Particularly preferred are high surface area "activated" carbons, such as those prepared by direct chemical activation. Petroleum Derived Carbons (by T. M. O'Grady and A. N. Wennerberg), American Chemical Society Symposium Series, Vol. 303, J. D. Bacha et al.,

eds., American Chemical Society Publications, Washington, D.C., (1986), may be consulted for further general and specific details on these activated carbons and their method of preparation. Preferably, the surface area of the activated carbon is at least 750 m²/g (measured by the BET method), preferably at least 800 m²/g, preferably at least 900 m²/g, 5 preferably at least 1000 m²/g, preferably at least 1200 m²/g; preferably no more than 2500 m²/g, preferably no more than 2200 m²/g.

Preferably activated carbon has an average particle size (e.g., a D50), just prior to combining with DCOIT or the marine coating formulation, of no more than 100 microns (0.1 mm), preferably no more than 50 microns, preferably no more than 40 microns, preferably no 10 more than 35 microns, preferably no more than 30 microns, preferably no more than 25 microns, preferably no more than 20 microns; preferably at least 5 microns, preferably at least 10 microns.

EXAMPLES

GERSTEL TWISTER polydimethylsiloxane (PDMS) coated stir bars were purchased from Gerstel GmbH. The paints used were Interlux MICRON 66 paint ("M66"), INTERSLEEK 970 paint ("P970") and INTERSLEEK 731 ("P731"), obtained commercially and mixed according to manufacturer's directions, except for the addition of DCOIT as described below.

Paint was mixed with DCOIT and adsorbent using orbital shaker (Red Devil Inc, USA) and applied on a Leneta paper or aluminum foil using a stainless steel gauge (wet film thickness 500 micrometer). Paint was dried overnight.

Paper on an appropriate support (20-40 sq.cm of paint surface) was immersed into 120 ml glass bottle containing 100 ml of artificial seawater, Twister stirring bar was inserted, and the bottle was placed on a stirring mixer. The stirring rate was 600 rpm. At day 1, 4, 7, 14, and 21, TWISTER bars were removed from bottles, wiped with paper towel and placed into HPLC vials containing 1 ml of acetonitrile. Adsorbed biocide was extracted at 35C for 30 min. After extraction bars were wiped again and returned back to a bottles with seawater/MAF paint. The concentration of biocides was measured by HPLC. Agilent 1200 HPLC equipped with autosampler, column heater and diode-array detector was controlled by Chemstation software. DCOIT was analyzed using Ultra C18 column 150x4.6cm (Restek Inc). The same isocratic conditions (70% acetonitrile, 2.3 ml/min) were used. DCOIT was detected at 280 nm. External standard technique was used for quantization of released biocides. Twister stirring bar capacity was estimated as 400 micrograms based on previous calibrations. Cumulative release of DCOIT is reported in weight percent, based on the weight of DCOIT in the coating composition.

Cumulative Release of DCOIT (% of total DCOIT released by indicated day)

Paint/DCOIT/carbon	Day 1	Day 3	Day 7	Day 14	Day 21
I731/1.2% DCOIT/4.8% SN-20	0.67	1.99	3.05	4.25	5.26
I731/1.2% DCOIT/4.8% RG-C	0.74	1.45	2.23	2.78	3.60
I731/1.2% DCOIT/4.8% HD	0.57	1.29	1.72	2.34	2.84
I731/1.2% DCOIT/4.8% CGP SUPER	0.64	1.42	2.37	3.33	3.81
I731/1.2% DCOIT/4.8% KB-G	0.74	1.68	2.54	3.46	4.53
Note: G-60 not compatible with I731 paint at 4:1 loading needed					
I731/2% DCOIT - Control	6.94	12.9	17.1	19.6	21.2
I970/1% DCOIT/2% G-60	4.53	8.91	13.3	16.7	20.2
I970/1% DCOIT/2% KB-G	2.28	4.78	6.99	8.64	10.9
I970/1% DCOIT/2% KB-WJ	2.82	5.09	7.85	11.2	13.1
I970/1% DCOIT/4% G-60	2.41	4.69	7.03	8.95	11.2
I970/1% DCOIT/4% KB-G	1.06	2.31	3.22	3.88	4.99
I970/1% DCOIT - Control	8.33	15.6	21.7	27.0	31.1
SPC /1% DCOIT/3% KB-G	1.57	4.60	6.53	8.40	11.1
SPC /1% DCOIT - Control	5.52	9.79	14.3	17.5	21.7
I731/1% DCOIT/3% KB-G	0.77	1.55	1.96	2.77	3.31
I731/1% DCOIT/3% S-51	3.25	6.06	7.93	9.27	10.2
I731/1% DCOIT/3% PAC 200	1.00	1.99	2.68	3.12	3.50
I731/1% DCOIT/3% HD	0.28	0.86	1.46	2.01	2.45
I731/1% DCOIT ---CONTROL	7.27	12.7	15.0	16.1	16.2
I970/1% DCOIT/3% KB-G	1.32	2.92	4.04	5.32	6.45
I970/1% DCOIT/3% S-51	2.33	4.03	5.92	7.70	9.41
I970/1% DCOIT/3% PAC 200	0.85	1.32	2.07	2.89	3.59
I970/1% DCOIT/3% HD	0.92	1.78	2.46	2.79	3.54
I970/1% DCOIT ---CONTROL	4.95	9.70	14.0	16.9	20.8

Notes:

DCOIT from SEANINE 211N biocide (Dow Chem. Co.), 30% DCOIT in xylenes

5 "SPC" paint is MICRON 66 paint (International Paints), wet thickness 254 microns

"I970" is INTERSLEEK 970 FRC paint (International Paints), wet thickness 127 microns

"I731" is INTERSLEEK 731 FRC paint (International Paints), wet thickness 127 microns

Activated Carbons

abbreviation	full name	surface area, m ² /g
HD	Nuchar HD	1500-1900
SN-20	Nuchar SN-20	1400-1800
RG-C	Nuchar RG-C	1400-1800
CGP SUPER	Norit CGP SUPER	1500-1700
KB-G	Darco KB-G	1700
KB-WJ	Darco KB-WJ	1800
G-60	Darco G-60	600
S-51	Darco S-51	650
PAC 200	Norit PAC 200	1000-1150

5 The data demonstrate that much better controlled release is obtained when DCOIT is combined with an activated carbon having a surface area greater than 650 m²/g.

CLAIMS

1. A composition comprising 4,5-dichloro-2-n-octylisothiazolin-3-one and an activated carbon having a surface area of at least 700 m²/g.
2. The composition of claim 1 in which a weight ratio of activated carbon to 4,5-dichloro-2-n-octylisothiazolin-3-one is from 1.5:1 to 10:1.
3. The composition of claim 2 in which the 4,5-dichloro-2-n-octylisothiazolin-3-one and the activated carbon are present in a marine coating.
4. The composition of claim 3 in which the marine coating comprises from 0.5 to 4 wt% 4,5-dichloro-2-n-octylisothiazolin-3-one and from 1.5 to 16 wt% activated carbon.
5. The composition of claim 4 in which the activated carbon has a surface area from 800 to 2500 m²/g.
6. The composition of claim 5 which the marine coating is a foul release coating.
7. The composition of claim 5 in which the marine coating is a self-polishing coating.
8. The composition of claim 7 in which the self-polishing coating is a metal acrylate copolymer coating.
9. The composition of claim 5 in which the weight ratio of activated carbon to 4,5-dichloro-2-n-octylisothiazolin-3-one is from 2:1 to 8:1.
10. The composition of claim 9 in which the marine coating comprises from 1 to 3.5 wt% 4,5-dichloro-2-n-octylisothiazolin-3-one and from 2 to 12 wt% activated carbon.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/067647

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09D5/16
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>WO 2009/045941 A1 (WORLD MINERALS INC [US]; GREENE MICHAEL [US]; LU JIE [US]) 9 April 2009 (2009-04-09) paragraph [0005] - paragraph [0015] paragraph [0051] - paragraph [0053] paragraph [0059] - paragraph [0061] paragraph [0066] - paragraph [0070] abstract; claims 1, 10, 11, 17, 18, 23-25, 42-44, 49-51; examples 1, 2; tables 1, 2 -----</p>	1-10
X	<p>US 2007/237738 A1 (HANZLICEK JENNIFER L [US] ET AL) 11 October 2007 (2007-10-11) paragraph [0005] - paragraph [0011] paragraph [0026] - paragraph [0028] abstract; claims 1-5, 26-31; examples 1-8 ----- -/-</p>	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

Date of mailing of the international search report

14 January 2014

22/01/2014

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/067647

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 142 477 A2 (ROHM & HAAS [US]) 10 October 2001 (2001-10-10) cited in the application paragraph [0007] - paragraph [0010] paragraph [0014] - paragraph [0017] paragraph [0019] - paragraph [0024] paragraph [0026] - paragraph [0032] abstract; claims 1-5, 7-10; examples 1-4; tables 1-4 -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/067647

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