

AD-D014 013

(1) DTIC FILE COPY

Serial No. 749,975

Filing Date 1 July 1985

Inventor(s) Robert F. Supcoe
Thomas Radakovich

NOTICE

The above identified patent application is available for
licensing. Requests for information should be addressed to:



Office of the Chief of Naval Research
Department of the Navy
Code OCCCIP
Arlington, Virginia 22217-5000

Accession For	
DTIC CRAFT	
DTIC TAB	
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	

DISTRIBUTION STATEMENT A	
Approved for public release:	
Distribution Unlimited	

DTIC
ELECTE
S 12 APR 1989 D
E

89 110

BIOCIDAL WAX COMPOSITION
AND PREPARATION THEREOFABSTRACT OF THE DISCLOSURE

A biocidal wax composition for preventing corrosion and biological fouling and surface degradation of submerged structures comprises from about 10 to about 40 percent of total biocidal wax composition of a biocidal polymeric gel consisting of a polymer from the group consisting of a polyethylene, polypropylene, a copolymer of polyethylene and vinyl acetate, and mixtures thereof and a solvent selected from the group consisting of mineral oil, a paraffin wax and mixtures thereof, and a biocide; and from about 60 to about 90 percent of total biocidal wax composition of a wax matrix composition consisting of petrolatum, at least two chlorinated waxes, and a microcrystalline wax. The biocidal wax is prepared by shock-cooling a hot solution of a polymer through its cloud point, admixing a biocide with the gel, and admixing the above wax matrix composition with the gel. Key words:

Patent applications, Antifouling Coatings,
Ship hulls, etc.

1 BIOCIDAL WAX COMPOSITION
2 AND PREPARATION THEREOF3 BACKGROUND OF THE INVENTION

4 This invention pertains generally to coatings and particu-
5 larly to bioactive wax coatings.

6 The drag of a ship's hull increases significantly from micro
7 to macro hard fouling which results from the attachment of
8 marine organisms, such as bacteria, algae and barnacles, on
9 the hull surface. Even after these organisms are removed,
10 the smoothness of the hull is seriously reduced by the pitting
11 caused by these organisms.

12 Other submerged structures experience deterioration caused
13 by marine growth or corrosion. Wooden blocks and piers can be
14 destroyed in a few years if left untreated. Many of the
15 traditional treatments, e.g., creosote, create serious environ-
16 mental problems. Metal structures, e.g., propellers and anchor
17 chains, lose appreciable performance capability or strength
18 through corrosion and marine growth on their surfaces.

19 One approach to reducing marine growth is coating the sur-
20 face with a coating toxic to marine organisms. The coating usually
21 comprises a matrix with one or more toxic materials in the matrix.

22 A frequently used type of matrix is resinous and forms
23 a paint. The disadvantages of paints are their expense, the
24 diminution of their effectiveness in time, the difficulty of
25 mechanically renewing the smoothness of the paint surface, and
26 the frequent corrosive effect of the toxic substances on the
27 metallic hull.

1 Instead of coating a hull with toxic paint, the hull can
2 be coated with non-toxic paint that is coated with a biocide-
3 containing wax. Toxic waxes are also used to renew toxic
4 paint surfaces after the paint has lost its toxicity. The
5 wax coating disclosed in U.S. Patent No. 4,020,200 by Groszek
6 et al. is typical, i.e., a wax with a stable biocide that
7 is insoluble in seawater but soluble in the wax. Another
8 example is the wax composition in U.S. Patent No. 4,115,130
9 by Crump et al. which also includes porous minerals to slow
10 the release of the biocide.

11 The rate of release is important to biocidal coatings
12 because if the biocide is released too quickly an environmental
13 problem is created and the coating becomes ineffective too
14 quickly. On the other hand, the rate of release must be
15 sufficient to maintain the required biocide concentration at
16 the surface of the submerged structure.

17 The wax compositions in U.S. Patent Nos. 4,410,363 and
18 4,293,339 by R. F. Supcoe and T. Radakovich utilize certain
19 halogenated waxes and wax combinations to provide superior
20 adhesion to a submerged surface and retention of the biocide
21 to provide a very durable and effective coating for retarding
22 marine growth on the submerged surface. The wax composition
23 in U.S. Patent No. 4,293,339 has the additional important
24 advantage of being capable of underwater application. The
25 other wax compositions require the removal of the surface
26
27
28

1 from the water or the water from the surface before an effective
2 coating on the surface is possible, i.e., a coating that is
3 smooth, continuous, uniform and strongly adhering. The dis-
4 advantage of the above wax composition is the use of one or
5 more fluoropolymers which greatly increases the cost of the
6 wax coating.

7 A biocidal wax coating that can adhere strongly to a
8 surface to form a smooth durable coating over a wide range
9 of temperatures, even if the wax is applied under water or on
10 a wet surface, is an important improvement in the technology.
11 If such a wax can be compounded without fluoropolymers,
12 the versatility and cost of this wax would permit a wide variety
13 of uses.

14 SUMMARY OF THE INVENTION

15 It is, therefore, an object of this invention to reduce
16 the maintenance costs for sea-going ships.

17 Another object is to improve the performance of ships
18 by reducing drag from a coarse and rough hull surface.

19 A further object of this invention is to apply a smooth
20 coating of a wax that contains a large amount of a slow-
21 releasing biocide to the surface of a submerged structure.

22 A still further object of this invention is to produce
23 strong adhesion by a bio-effective wax to a submerged structure.

24 These and other objects are achieved by a biocidal wax
25 comprising a biocide-containing polymeric gel that is dispersed
26
27

1 in a microcrystalline-chlorinated paraffin wax matrix. The
2 polymeric gel permits a high biocide loading of the wax and
3 produces an effective release rate. The wax matrix is able
4 to displace water molecules on a wet surface, spread easily,
5 and form a uniform and durable coating.

6 DETAILED DESCRIPTION OF THE INVENTION

7 The wax compositions of this invention comprise several
8 types of waxes: paraffin waxes, microcrystalline, and chlorinated
9 waxes. Each type contributes a needed property to the final
10 wax coating or its application. Unlike the wax composition of
11 U.S. Patent No. 4,293,339, which has extremely hydrophobic
12 fluorinated compounds, these waxes also must be optimized
13 for underwater application and compatibility to prevent separa-
14 tion over the operational temperature range.

15 A paraffin wax refers to the waxes derived from the wax-
16 distillate fraction of crude petroleum and has a molecular
17 weight from about 260 to about 460 and a melting point from
18 about 49°C to about 60°C. Paraffin waxes improve spreadability,
19 but are not durable. The principle purpose of a paraffin
20 wax in the subject wax compositions is to be a solvent for the
21 polymer in the biocidal gel. The preferred paraffin waxes
22 have a melting point from 55°C to 60°C and a molecular weight
23 from 260 to 350.

24 Microcrystalline waxes are derived from the heavy lubri-
25 cating-oil fractions of the petroleum distillate. A micro-
26 crystalline wax has an average molecular weight from about 400
27 to about 700, has from about 40 to about 50 carbon atoms,
28

1 and a melting point above about 65°C. A microcrystalline wax
2 is generally tough but difficult to spread. The presence of a
3 paraffin wax, for example, would compensate for the low plasticity
4 of a microcrystalline wax. Petrolatum is a two-phase colloidal
5 system or gel consisting of high molecular weight hydrocarbon oils
6 dispersed in microcrystalline waxes. Composition and physical
7 properties vary considerably and so petrolatum is described by
8 its physical properties.

9 Chlorinated waxes (chlorowaxes) are short-chain chlorinated
10 aliphatic saturated hydrocarbons. The properties of a particular
11 commercial chlorinated wax depend on the nature of the starting
12 paraffin, the chlorine content and the manufacturing process.
13 The chlorinated waxes of this invention have, on an average,
14 from about 10 to about 30 carbon atoms and a chlorine content
15 from about 40 to about 70 percent. It has been determined that
16 a mixture of chlorowaxes produce significantly better results
17 than a single chlorowax. Exemplary of commercially marked
18 chlorinated waxes are Chlorowax (Diamond Shamrock) and Cereclor
19 (Imperial Chemical Industries, Ltd.).

20 For an effective application of a biocide-containing wax
21 with a high biocide concentration underwater or on a wet surface,
22 it is necessary to combine the biocide with a polymeric, i.e.,
23 nonwax, gel. The polymeric gels found to hold a high concentra-
24 tion of the biocides of this invention and be compatible with
25 the wax matrix of the subject compositions are gels of poly-
26 ethylene, polypropylene, a copolymer of polyethylene-vinyl
27 acetates and mixtures thereof.

1 The polyethylene and polypropylene polymers are non-polar,
2 branched but crystalline thermoplastics and are referred to as
3 low density. The polyethylene is typically prepared by free-
4 radical bulk polymerization of the monomers under high pressure.
5 The chain can contain many long or short branches and their
6 number affects the polymer density. For compositions of this
7 invention, the molecular weight is from 12,000 to 25,000 and a
8 density from 0.90 to 0.93g/cc. The copolymers have a vinyl
9 acetate content from 15 to 30 percent with 19 to 28 percent
10 preferred. The preferred solvents are mineral oil and short-
11 chain or paraffin waxes with a melting point below about 25°C.

12 The gels are prepared by shock-cooling a hot polymer
13 solution through the cloud point which is the temperature
14 at which a hot relatively clear solution of a polymer becomes
15 cloudy or fairly opaque upon cooling. The hot polymer solution
16 is preferably prepared by admixing a polymer with a solvent at
17 a temperature at least 5°C above the cloud point and preferably
18 from about 5 to 15°C above the cloud point. The solution is from
19 about 85 to 100 percent concentrated and preferably from 95 to
20 100 percent concentrated. Subsequent cooling to room temperature
21 causes the complete precipitation of the polymer in the form of
22 a fine-particle gel. The cooling through the cloud point should
23 be extremely rapid.

24 The change from solution to the colloidal state occurs
25 between about 5 and 10°C below the cloud point. It is in the
26 range from the cloud point to the change of state that the
27
28

1 cooling rate has an effect on the quality of the gel. Shock
2 cooling can be achieved in several ways, e.g., by cooling
3 the solution quickly in thin layers as on a three-roll mill,
4 by the addition of a cold solvent to the hot solution, or by
5 addition of the hot solution to a cold solvent. The use of
6 the cold solvent of the solution to shock cool the solution is
7 preferred in order to prevent contamination problems. The
8 biocides that are suitable for the biocidal gels and wax
9 compositions of this invention are organotin polymers or poly-
10 siloxanes, toxic copper compounds such as copper oxide and
11 copper-2-ethyl hexoate, and chlorinated compounds. Since a
12 major constituent of the wax matrix is one or more chlorinated
13 waxes, the preferred biocides are chlorinated compounds, such
14 as 4-chloro-m-cresol, p-dichlorobenzene, 2,3,4,6-tetra-chloro-
15 4-(methyl-sulphonyl) pyridine, tetrachloroglycoluril, dichloro-
16 phen, and 2,4,5,6 tetrachloroisophthalonitrile. The most
17 preferred biocide is the above tetrachlorophthalonitrile.

18 The amount of biocide to be added to the gel is from about
19 15 to 50 weight percent of the total weight of the resulting
20 biocidal gel. Since one of the purposes of the gel is to maximize
21 the loading of the biocide in the wax composition, the preferred
22 amount of biocide is from 40 to 50 weight percent of the biocidal
23 gel and, of course, the most preferred would be 50 percent of the
24 gel weight. A 50 weight percent concentration is equal to the
25 inclusion of a biocide equal in weight to the gel, i.e., a 100%
26 loading of the gel.

27 The wax matrix composition comprises petrolatum in an amount
28 from about 20 to about 37 weight percent and preferably from 25

Navy Case 66,145

1 to 33 weight percent; one or more chlorinated waxes in an amount
2 from about 40 to 60 weight percent and preferably from 45 to 55
3 weight percent; and a second microcrystalline wax in an amount
4 from about 10 to about 25 weight percent and preferably from 12 to
5 18 weight percent.

6 Petrolatum has a melting point from about 48°C to about 57°C
7 (ASTM D 127), a viscosity at 99.5°C from about 60 to about 75 SUS,
8 and a consistency at 25°C (ASTM D 937) from about 140 to about
9 240. This petrolatum is classified as a white petrolatum.

10 The best and most consistent results for underwater applica-
11 tions have been obtained with a particular blend of chlorinated
12 waxes. It is theorized that this particular blend is so effective
13 because each wax compensates the others in terms of either the
14 ability to displace water molecules at the submerged or wet sur-
15 face or toughness of coating. The chlorinated wax composition
16 comprises from about 16 to 26 weight percent of a chlorinated
17 wax having an average number of carbon atoms from about 11 to
18 about 13 and a chlorine content from about 65 to 70 percent,
19 from about 8.5 to about 11.5 weight of a chlorinated wax having
20 an average number of carbon atoms from about 22 to about 26 and
21 a chlorine content from about 39 to 45 percent, from about 8
22 to 12 weight percent of a chlorinated wax having an average
23 number of carbon atoms from about 11 to 13 and a chlorine content
24 from about 55 to about 65 percent, and from about 9 to 13 weight
25 percent of a chlorinated wax having an average number of carbon
26 atoms from about 18 to about 22 and a chlorine content from about

Navy Case 66,145

36 to about 44 percent. The preferred composition for the chlorinated wax blend comprises from 21 to 23 weight percent of a chlorinated wax having an average number of carbon atoms of 11.5 and 12.5 and a chlorine content from 68 to 70 percent, from 9 to 11 weight percent of a chlorinated wax having an average number of carbon atoms from 23 to 25 and chlorine content from 41 to 44 percent, from about 9 to 11 weight percent of a chlorinated wax having an average number of carbon atoms from 11.5 to 12.5 and a chlorine content from 58 to 62 percent, and from 10 to 12 weight percent of a chlorinated wax having an average number of carbon atoms from 19 to 21 and a chlorine content from 38 to 42 percent. The above weight percentages are percentages of the wax composition weight.

Other chlorinated wax combinations or a single chlorinated wax proxuce a coating that is not as uniform and strong or has a more limited operating range as a coating produced by this particular wax combination if the coating is applied underwater. If the surface is not underwater or very wet, these other wax formulations would be extremely effective because of the high biocide content and favorable biocide release rate of the polymeric gel.

A second microcrystalline wax is included in the overall wax formulation. This wax is a typical microcrystalline wax which accordingly increases the hardness and durability of the wax coating. The preferred wax has a melting point from about

Navy Case 66,145

1 65°C to 72°C (ASTM D-127-30), a specific gravity at 15.5°C is
2 from 0.91 to 0.92, a Saybolt viscosity at 99°C from 65 to 85, and
3 a penetration from 25 to 35 as determined by ASTM D-5-25. The
4 amount of this microcrystalline wax is from about 10 to about 18
5 weight percent and preferably from 13 to 16 weight percent of the
6 total biocidal-wax-composition weight.

7 The amount of the wax matrix composition is from about 60
8 to about 90 percent of the total biocidal wax composition
9 weight and preferably from 65 to 75 weight percent. Accordingly,
10 the amount of the biocidal gel is from about 10 to 40 percent
11 of the total biocidal wax composition and preferably from 25
12 to 35 weight percent.

13 An anionic surfactant can be added to enhance the wetting
14 ability, i.e., the ability to displace water molecules on
15 the surface to be treated. The amount of surfactant can be as
16 high as about three percent of the total biocidal-wax-composition
17 weight; however, the usual amount is from 0.5 to 2 weight percent
18 of the total wax composition. Examples of anionic surfactants
19 are amine salts of carboxylic acids.

20 The biocidal wax composition is prepared by preparing a
21 polymeric gel in the manner previously described; mixing in
22 a biocide to form a biocidal gel; preparing a wax mixture of
23 petrolatum, chlorinated waxes, a second microcrystalline wax,
24 and any surfactant; heating the wax mixture to a temperature
25 from about 50 to about 60°C and preferably from 52 to 56°C;
26 admixing the wax mixture and the biocidal gel to form the
27 biocidal wax, and mixing the biocidal wax while the wax cools to
28 room temperature, (about 20°C).

1 For large surfaces, such as a large hull, the biocidal wax
2 composition is preferably applied underwater by spraying.
3 Preferably, the wax is applied at a temperature from about 40°C
4 to 70°C, and most preferably from 50°C to 60°C. A spraying
5 pressure from about 60 psi to about 150 psi is preferably used
6 in order to ensure that the wax fills most small cracks, nicks
7 and other minor imperfections in the surface rather than coat
8 over the imperfections. Special spraying equipment must be used
9 in order to minimize waste and pollution.

10 It is preferred for intermediate surfaces to apply the wax
11 underwater with a brush or wide flat applicator, such as a
12 hard foam material. For a small application, e.g., a propeller
13 on a small ship, a simple cloth can be used. It has been
14 determined that an anchor chain can be easily coated by brush,
15 as the anchor is raised and the chain, in turn, coats the metal
16 sprocket, drum and other metal parts of the anchor raising
17 mechanism.

18 Having described the invention in general. the following
19 examples are given by way of illustration and are not meant
20 to limit this disclosure or the claims to follow.

21 EXAMPLE I

22 PREPARATION OF BIOCIDAL WAX 20N

23 Mineral oil (500ml) was heated to 45°C and polyethylene
24 with an average particle size of about 4 micrometers was added
25 to the mineral oil until a saturated solution was obtained.
26
27
28

Navy Case 66,145

1 The heated solution was poured into 800 ml of mineral oil at a
2 temperature of 10°C to form a viscous gel. The gel was separated
3 by carefully removing excess mineral oil. To 500 grams of gel,
4 at 22°C, 100 grams of 2,4,5,6 tetrachloroisophthalonitrile
5 Nopocide N96 by Diamond Shamrock Corporation) was added and
6 mixed.

7 A wax mixture (700 grams) was prepared by admixing 210 grams
8 of petrolatum, 161 grams of a chlorinated wax with a molecular
9 average of 12 carbon atoms and 70% chlorine content (Chlorowax
10 70L), 70 grams of a chlorinated wax with a molecular average
11 of 24 carbon atoms and 42 percent chlorine content (Chlorowax 40),
12 70 grams of a chlorinated wax with a molecular average of 12
13 carbon atoms and a chlorine content of 60 percent (Chlorowax 500),
14 84 grams of a chlorinated wax with a molecular average of 20
15 carbon atoms and a chlorine content of 40 percent (Chlorowax 100),
16 105 grams of a microcrystalline wax (Indramic 30), and 14 grams
17 of a black dye (for determining the quality of the wax coating).
18 The wax mixture was mixed at 52°C and 300 grams of the biocide
19 gel was added and mixed. While mixing was continued, the wax
20 mixture was allowed to cool to room temperature.

21 EXAMPLE II

22 PREPARATION OF BIOCIDAL WAX 60N

23 The procedure of Example I was repeated except that
24 300 grams of Nopocide was added instead of 100 grams.

25

26

27

28

EXAMPLE III

PREPARATION OF BIOCIDAL WAX 100N

The procedure of Example I was repeated except that 500 grams of Nopcocide was added instead of 100 grams.

EXAMPLE IV

PREPARATION OF BIOCIDAL WAS 80C

The procedure of Example I was repeated except that 400 grams of cuprous oxide was added instead of 100 grams of Nopcocide.

EXAMPLE V

PREPARATION OF BIOCIDAL WAX F-1

The procedure of Example I was repeated for the preparation of an 80 percent loading of Nopcocide, i.e., 400 grams of Nopcocide to 500 grams of mineral oil. The wax composition comprised 210 grams of Petrolatum, 385 grams of Chlorowax 70L, 105 grams of Indramic, and 14 grams of dye. The wax composition was heated to 55°C, the biocidal gel was added, the mixture was mixed, and it was allowed to cool to temperature.

EXAMPLE VI

PREPARATION OF BIOCIDAL WAX F-2

The procedure of Example V was repeated except that 385 grams of Chlorowax 500 were added instead of Chlorowax 70L.

EXAMPLE VII

PREPARATION OF BIOCIDAL WAX F-3

The procedure of Example V was repeated except that 150 grams of petrolatum were added instead of 210 grams and 245 grams of Chlorowax 40 and 200 grams of Chlorowax 500 were added instead of 385 grams of Chlorowax 500.

EXAMPLE VIII

APPLICATION OF EXAMPLES I - VII
ON A SUBMERGED SURFACE

Seven steel plates (10cm x 15cm) were placed in a pan of water at a temperature of about 2°C. Each plate was coated with a wax of the seven previous examples by wiping on the wax with a temperature of 55°C. The wiping was done in a back and forth manner.

The waxes from Examples I - IV were easy to apply and an inspection of the plates showed that the coatings were uniform and complete. Waxes from Examples V and VII were difficult to apply. Often the wax would ball up when the cloth moved in the direction opposite to the direction of application. Visual inspection showed that the coatings were not uniform. The wax from Example VI was difficult to apply and the wax coating was not as uniform as those of the first examples, but was judged to be overall better than the waxes of Examples V and VII.

EXAMPLE IX

DURABILITY OF WAX COATINGS

Ten stainless steel, mild steel and bronze plates (10cm x 15cm) were coated with the wax of Examples II in the same manner of Example VIII. The plates were suspended by steel chains in the brackish water of the Severn River in the month of October at a pier at the David Taylor Naval Ship Research and Development Center (DTNSRDC) at Annapolis, Maryland. The steel chains were coated with the above wax while they were in the river. After 180 days the plates and chains were visually inspected and no sign of corrosion or marine infestation was evident.

EXAMPLE X

DURABILITY OF WAX COATING ON HULL OF SHIP

The stainless steel propeller of 70-foot boat at DTNSRDC was coated by brush of a wax from Example III while the propeller was in the Severn River. The wax was 23°C at the time of application. The propeller was operated about 35 hours over 180 days. Sufficient wax remained to prevent any visible marine infestation at the end of the test.

These examples show that the subject wax compositions can have a high biocide loading, the waxes can be easily applied under water, the wax coatings are durable, and the coatings have an effective leach rate.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings.