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(54) ANTIFOULING COATINGS FOR SURFACES IN CONTACT WITH WATER

(71) We, AB EXTENSOR, a Swedish Company, of Box 323, 181 03 Lidingö, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the prevention of fouling of surfaces in contact with fresh or salt water.

A ships bottom or other surface that requires protection against adherence of organisms that can grow on surfaces submerged in water is, according to the invention, provided with an anti-fouling coating comprising a fluorocarbon polymer and an anti-fouling agent that can counteract growth of organisms on surfaces submerged in water.

Such a coating can be formed by applying to the surface a dispersion in a liquid dispersion medium of particles of the fluorocarbon polymer and the antifouling agent. The medium preferably includes a liquid halogenated hydrocarbon. The preferred compositions comprising liquid halogenated hydrocarbon are novel and are described and claimed in Application No. 49086/77 (Serial No 1598091) from which the present application is divided.

The fluorocarbon polymer must contain fluorine bonded to a carbon chain in a polymer. Fluorine may be the only halogen in the polymer but other substituents may be present in the polymer, for instance chlorine. Polytetrafluoroethylene is the preferred fluorocarbon polymer but others that may be used include tetrafluoroethylene - perfluoropropylene, fluoroethylene - propylene and ethylene - tetrafluoroethylene copolymers, polytrifluorochloroethylene, polyvinyl fluoride, polyvinylidene fluoride, fluorinated rubber, e.g. products made by vulcanising polychlorotrifluoroethylene and/or vinylidene fluoride - hexafluoropropylene copolymers with polyfunctional amines or peroxides, and fluorinated silicone rubber, especially peroxide - vulcanised.

Further fluorocarbon polymers which can be used according to the invention and which may or may not contain hydrogen, chlorine, nitrogen or other atoms or groups in the repeating groups or included in other ways in the molecule, are disclosed in the book "Fluoropolymers, Leo A. Wall, Wiley - Interscience (High Polymers Vol. XXV, Library of Congress Catalog Card Number: 74—165023).

The fluorocarbon polymer when introduced as a dispersion, can be in the form of fine particles, for instance with a particle size less than 20 microns and often with a particle size below 10 to 15 microns. The majority of the particles or all the particles often have a particle size exceeding 0.1 to 1 micron. Preferably the average particle size is approximately 5 microns. The shape of the particles may be essentially spherical, blocky, flaky, or fibrous with the diameter size stated above.

The density of the polytetrafluoroethylene may be 2.14—2.20, preferably approximately 2.16 grams per cc. The melting point (crystal) suitably is 280—330°C, particularly approximately 300°C. The average molecular weight may vary within a wide range, for instance

1,000—20,000 and preferably 2,000—5,000, e.g. approximately 3.700.

The softening point (ASTM E-28—58-T) may vary, for instance between 240 and 280°C, for instance approximately 265°C.

Fluorocarbon polymers often are offered as a dispersion in suitable dispersion media, for. instance chlorinated or fluorinated hydrocarbons, for instance fluorinated hydrocarbons such as those sold under the product name of "Freon". One example is trichlorotrifluoroethane. "Freon" is a registered Trade Mark.

The amount of fluorocarbon polymer in the coating may vary within broad limits depending on the amount of anti-fouling compounds and other substances, for instance binders. Measured on the weight of the dry coating the fluorocarbon polymer weight may be up to 95%, preferably up to 50% and in many cases up to 25%. Also amounts up to 5—10% are usable. The lower range varies as well depending on the other ingredients and on the demands. A lower range between 10 and 25% is often preferable but even lower amounts are usable, for instance down to 5% and even down to 1%. The preferred compositions contain 10 to 50% by weight of the polymer, based on the dry coating weight.

The anti-fouling agent is an agent which when included in the coating prevents or retards the adherence to and growth on the coating of organisms which live in water, e.g. bacterial or diatome slimes, algae, barnacles, mussels, tube or ship worms, moss, teredos, limnoria, martesia, sphaeroma, oysters and bryozoans.

The anti-fouling agent can be selected from a wide number of substances that are known to counteract growth of organisms on surfaces, including surface coatings, submerged in sea or other waters. Suitable substances are described in, for instance, U.S. Patent Specifications Nos. 3,787,217, 3,854,960 and 3,912,519 and reference should be made to those.

The preferred anti-fouling agents for use in the invention are metallic copper in powder form as well as copper oxide, for instance Cu_2O, as well as other copper compounds, arsenic compounds, mercury compounds and solid chlorinated hydrocarbons, for instance hexachlorocyclohexane and also tin compounds, particularly triorganotin compounds, for instance tributyl- and triphenyl tin compounds, e.g. tributyl tin oxide.

Although these are often preferred a wide range of anti-fouling agents can be used. As examples of antifouling agents the following may be mentioned:

Organic and inorganic compounds of one or more elements belonging to the following groups of the periodical system: 2a (Be, Mg, Ca, Sr, Ba), 3b (Se, Y, La, Ce, Th), 4b (Ti, Zr, Hf), 5b (V, Nb, Ta, U), 6b (Cr, Mo, W), 7b Mn, Tc, Re), 8 (Fe, Ni, Co), 1b (Cu, Ag, Au), 2b (Zn, Cd, Hg), 3a (B, Al, Ga, In, Tl), 4a (C, Si, Ge, Sn, Pb), 5a (P, As, Sb, Bi), 6a (S, Se, Te), 7a (F, Cl, Br, J), as well as the other lanthanides, and also several of the elements stated above in elemental state.

Examples are organic and inorganic heavy metal compounds, such as zinc oxide, zinc thiocarbamate, zinc carbonate, zinc metal, lead metal, lead acetate, phenolic lead compounds phenyl-lead compounds, phenols and phenolic compounds, phenyl compounds, such as phenyl-metal compounds, e.g. phenyl-heavy metal compounds, phenyl-urea compounds, e.g. according to the Swedish patent No. 7106810—0, triazine derivates, e.g. combined with heavy metal compounds, e.g. tin, zinc, lead, copper compounds, triphenyl arsazine chloride, chinoxaline derivate, solid chlorinated hydrocarbons, e.g. DDT, pentachlor phenol, naphthenates, e.g. Cu, Zn, Fe naphthenates, formaldehyde, paraformaldehyde.

Further examples of antifouling agents are disclosed in the U.S. patents Nos. 3,676,388, 3,266,913, 3,885,039, 3,100,718, 3,100,719, 3,794,501 and the Swedish patent publications Nos. 334,613, 140,806, 213,824, 353,343, 381,275, 7206111—2, 370,082, to which reference should be made.

Further examples of antifouling agents which can be used in antifouling compositions according to this invention are:

Cuprous oxide, copper powder, mercury oxide, cuprous oxide - mercury oxide (e.g. in the ratio 3:1), mercurous chloride, organic tin compounds, e.g. triphenyl tin chloride, triphenyl tin bromide, tri-p-cresyl tin chloride, triethyl tin chloride, tributyl tin chloride, phenyldiethyl tin fluoride, tri - (p - chlorophenyl tin) chloride, tri - (m - chlorophenyl tin) chloride, dibutylethyl tin chloride, dibutyloctyl tin bromide, tricyclohexyl tin chloride, triethyl tin stearate, tributyl tin stearate, triethyl tin fluoride, tributyl tin fluoride, diphenyl tin chloride, diphenylethyl tin fluoride, triphenyl tin hydroxide, triphenyl tin tiocyanate, triphenyl tin trichloroacetate, tributyl tin acetate, tributyl tin decanate, tributyl tin neopenthanate, trioctyl tin decanate, tributyl tin oxide, trioctyl tin oxide, triphenyl tin fluoride, tributyl tin oleate, tripropyl tin neodecanate, tributyl tin laurate, tributyl tin octanoate, tributyl tin dimethylcarbamate, tributyl tin resinate, tributyl tin chromate, amyldiethyl tin decanate, tributyl tin naphthenate, tributyl tin isooctylmercapto acetate, bis(tributyl tin) oxalate, bis(tributyl tin) malonate, bis(tributyl tin) adipate, bis(tributyl tin) carbonate, organic lead compounds, e.g. triphenyl lead acetate, triphenyl lead stearate, triphenyl lead neodecanate, triphenyl lead oleate, triphenyl lead chloride, triphenyl lead laurate, triethyl lead oleate, triethyl lead acetate, triethyl lead stearate, trimethyl lead stearate, triphenyl lead bromide, triphenyl lead fluoride, organic compounds, such as 10,10' - oxybisphenoxazine (SA—546), 1,2,3 - trichloro - 4,6 - dinitrobenzene, hexachlorophene, dichlorodiphenyl trichloroethane, phenolmercury acetate, tetrachloroisophthalonitrile, bis(n - propylsulphonyl) ethylene, and N - dimethyl - N' - phenyl - (N' - fluorodichloromethylthio) sulphamide.

Anti-fouling agents that are particularly effective against balanides and other barnacles, mussels and tubifex include mixtures of Cu_2O and HgO.

When copper powder is used as the anti-fouling agent it may be approximately 300 to 30 standard mesh for instance 50% "fine" and 50% "superfine", e.g. from 0.02—0.04 mm to 0.5—1 mm particle size. Preferably flaky particles are used with a ratio thickness/diameter of 1/10 to 1/100, preferably 1/20—1/50, at least 50% and preferably at least 80% of the particles having a diameter below 10 microns.

It is particularly preferred that the coating comprises polytetra fluoroethylene together with copper powder and/or Cu_2O.

The amount of anti-fouling agent may be varied within a very wide range. The coating may contain, measured on dry weight, up to 90—95% anti-growth compounds, suitably up to 50% and particularly up to 25%. Also lower amounts, for instance up to 5 or 10%, are suitable for certain types. The lowest effective amount varies depending on the type of compound and may for instance range between 5 and 10%. Even lower amounts, for instance down to 1 or 0.1% are suitable. Generally the amount is from 5 to 50%.

As previously mentioned, the coating may be formed from a dispersion in a liquid dispersion medium which preferably comprises liquid halogenated hydrocarbon in an amount of at least 10% by weight of the composition. The dispersion medium can be removed by evaporation or by dissolution. Suitable halogenated hydrocarbons include halogenated alkane and halogenated alkylene hydrocarbons, e.g. chlorinated and/or fluorinated hydrocarbons, e.g. methylene chloride, trichloethane, trichlorethylene and "Freon" - hydrocarbons, for instance hydrocarbons with 1, 2, 3 or 4 carbon atoms in the chain with at least 25, 50, 75 or 100% of the hydrogen atoms substituted with fluorine and optionally chlorine, especially trifluorotrichlorethane. Other liquids may be included in the dispersion medium and may be polar or non-polar. Thus the dispersion medium may include hydrocarbons (including aromatic hydrocarbon solvents), alcohols (preferably alkanols containing 1 to 4 carbon atoms), ketones with 2 to 8 carbon atoms or water. Thus a dispersion of the fluorocarbon and anti-fouling agent in the dispersion medium comprising liquid halogenated hydrocarbon may itself be dispersed or blended into water.

The dispersing medium preferably comprises one or more constituents selected from trifluorotrichloroethane, trichloroethylene, trichloroethane and methylene chloride optionally with one or more constituents selected from toluene, alkanols containing 1 to 4 carbon atoms and acetone, with the preferred dispersion media consisting of trichlorotrifluoroethane, preferably in an amount of above 50%, together with one or more of toluene, n - heptane or, especially trichloroethane.

The amount of dispersion medium is generally from 10 to 95% and is preferably at least 20 and most preferably at least 40%. Generally the amount is from 40 to 75%, the percentages being by weight based on the total weight of the dispersion.

The compositions may contain for instance additional amounts of binders, pigments, fillers and other additives especially pigments with a layer lattice structure.

Useful binders are for instance epoxy resins and other binders of a thermoplastic or of a curable type, which are suitable in combination with fluorocarbon polymers. A number of such materials are described in the literature, for instance in the Swedish patent publication 219,806 to which reference should be made. As examples such curable and non-curable plastics as phenolic resins, urea-formaldehyde plastics, alkyd plastics, epoxy plastics, polyurethane plastics and alkyl silicone plastics and silicones may be mentioned.

As an example of a suitable pigment with particular characteristics pigments with layer lattice structure can be mentioned, for instance molybdenum disulphide, MoS_2 and graphite. A suitable amount of these substances is from 0.1 up to 5 or 10% by weight of MoS_2 which together with polyfluorocarbons gives a special effect and contributes also to reducing the friction as well as increasing the speed. Graphite can also be used as a substitute for or in combination with MoS_2.

The coating may include colloidal silicon dioxide gel, for instance of the type that is produced by flame hydrolysis of silicon compounds.

The coating may include organic silicone compounds which may be of the oil-type or resin-type and may be curable or non-curable (thermoplastic) linear or tridimensionally linked. Silicones are discussed thoroughly e.g. in a book by W. Noll: "Chemie und Technologie der Silicone", second addition, Verlag Chemie, Weinheim, BRP, 1968 and in "Chemie und Technologie der Kunststoffe", volume II, Akademische Verlagsgesellschaft Geest & Portig K-G, Leipzig, 1963, pages 789—858 and in 'Silicone Technology", editor: Paul F. Bruins (Applied Polymer Symposia no. 14), Interscience Publishers, John Wiley & Sons, New York. Also suitable silanes, preferably those which can form silicone polymers or siloxanes (polysiloxanes) may be included in compositions according to the invention.

The molecular weight of the silicon organic compounds used according to the invention may vary within broad limits, e.g. up to 100,000, preferably up to 10,000.

The content of silicon organic compound (including polymers) may vary, based on the solids weight (dry weight) from zero up to 5%, preferably from 0.01%, especially 0.1%, and particularly 0.3% up to 3%, especially up to 1%.

The silicon organic compounds may also partly substitute the fluorocarbon polymers in compositions used in the invention. The silicon organic compounds may consist of the silanes, siloxanes, silicones including linear or three-dimensionally linked polymers of the compounds mentioned above.

The compositions from which the coatings are formed may be formulated in various manners, for instance as one component compositions or as multi-component compositions. A suitable type is a 2-component composition comprising a fluid component containing fluorocarbon polymers dispersed in solvents optionally together with binders, and a pigment component containing anti-fouling compound or compounds optionally together with other additives and optionally dispersion media. Preferably the pigment component is a solid powder and is mixed with the liquid component prior to use. Suitable for instance is a liquid component containing as main ingredients a fluorocarbon polymer dispersion and solvent, preferably approximately 20% of a fluorocarbon polymer, e.g. of the same type as "Teflon" (a registered Trade Mark) (polytetrafluoroethylene) for instance with a fluorocarbon polymer content of 20—80% and as balance a liquid dispersion media, for instance of the "Freon"-type plus approximately 80% additional solvents, for instance trichloroethylene or similar (for instance "Chlorthene Nu" (a registered Trade Mark) which is sold by Dow Chemicals). The liquid component may furthermore contain binders of other types, for instance those mentioned above. The pigment constitution can e.g. comprise copper powder in an amount of 50—90% and molybdenum disulphide in an amount of 10—15%, for instance approximately 70% copper powder and 25% molybdenum disulphide. The weight ratio of the liquid component to the pigment component can be approximately 25—200 g pigment per 800—975 g of the liquid component and approximately 125 g pigment with the previously mentioned composition of fluids, fluorocarbon polymer containing component and pigment component.

It is sometimes preferred to select as the dispersion medium one or more materials which will partially dissolve the fluorocarbon polymer, for instance in an amount up to 25%, generally 1 to 15% or most preferably 10% although in some instances it may be desirable to dissolve only, for instance, 0.1 to 1% of the polymer. The dissolution may be partial so that the polymer is only swollen or it may form a type of colloid.

The coatings may be applied in different manners, for instance with a paint brush, a roller, by spraying, dipping, flow coating.

Instead of applying from a dispersion the coating may be melted or sintered on the surface by heating. For polytetrafluoroethylene, suitable temperatures are over 280°C, such as 300—315°C, for 1—20 minutes, for instance 5—10 minutes. Flame spraying can also be used for forming the coating.

The coatings may be formed on various substrates, for instance steel, zinc, aluminium, stainless steel, plastic, concrete, stone (silicate) glass, porcelain, artificial stone, brick, wood, with or without precoatings of paint, lacquer and phosphate or chromate conversion coatings.

It is also possible to form the coating on a surface that has been prepared or pretreated in some well known manner, for instance with conversion coatings such as phosphate treatments, chromate treatments, oxalate treatments and similar, as well as prepared with prior coatings of paint type products that contain binder compositions. A number of such pretreatment compounds or paint type compositions are well known, e.g. primers.

The thickness of the applied coating may vary. Usually, a coating thickness less than 50 microns may be used, particularly less than 25 microns, for instance less than 10 or 5 microns. A normal lower thickness range is 1—5 microns and a preferred thickness range is between 5—15 microns. The amount of anti-fouling compounds, for instance copper powder or copper oxide, may correspondingly vary for instance up to 50 g/m^2, particularly up to 25 g/m^2, for instance up to 10 or 15 g/m^2. A suitable lower range is often between 1 and 5 g/m^2 but even lower amounts, for instance 0.1 g/m^2 can be used. An amount of 25—75%, preferably approximately 50% of the binder weight is often suitable, for instance for copper powder, Cu_2O and similar.

The compositions can also contain etching components such as phosphoric acid and other acid or alkaline components, which attack the substrate and improve the adhesion. These components can be of the "Wash-primer" type and can also include for instance zinc chromate or other chromates and polyvinyl butyral and similar constituents known from Wash-primers. Other usable constituents, e.g. in compositions containing water as a dispersing or emulsifying vehicle, are thermoplastic constituents such as acrylic monomers copolymerised with other unsaturated monomers, polyvinyl acetate, polystrene, vinylchloride - vinylidene chloride copolymers, other vinyl polymers, styrene - butadiene copolymers, chlorinated rubber, colophonium - resinates, linear polyesters such as polyethylene terephthalate, polybutylene terephthalate, polyisobutylene and rosine.

As further examples of pigments and fillers, rust- and corrosion-protective additives such as red lead, zinc chromate, metallic zinc, metallic aluminium powder, and metallic aluminium bronze powder can be used.

In the coating composition or in the coating, filler particles may be included, e.g. particles which improve the resistance or strength of the coating. Particles of inorganic or organic materials can be used, such as molten or sintered water resistant materials, e.g. glass, ceramic materials and metals. The shape of the particles may be regular, e.g. spherical, such as glass beads, plastic beads, or irregular, such as flaky, fibrous, blocky and shapes obtained by crushing, etc. The filler particles may also comprise the antifouling agent and/or fluorocarbon polymer included or bonded to the surface of the filler particles. The filler may also consist of a pigment material.

When using beads of glass or resin, e.g. vinylic or acrylic resin or an elastomeric material such as rubber a diameter of 1—100 microns, preferably 5—50 microns or 5—30 microns may be suitable. The beads can be included for improving the friction characteristics of the coating in water.

Example.

A coating composition with the following constituents was prepared:

100 grams polytetrafluoroethylene average molecular weight about 5000

100 grams copper powder, flaky, 80% below 10 microns in diameter

30 grams molybdenum disulphide

the polytetrafluoroethylene was dispersed in 770 grams of a mixture of 200 grams trifluorotrichloroethane and 570 grams trichloroethane and the other constituents were then dispersed in said dispersion. This composition was applied to a film thickness of 5—10 microns on ship bottoms of plastics, aluminum and steel with and without undercoatings of paint and gave a good long time effect against fouling in sea-water.

The bonding of said coating to the substrate can also be improved in a per se well-known manner, e.g. with a primer coating, e.g. of the types mentioned above, such as an epoxy primer, the antifouling composition coating being applied when the primer coating still gives a bonding effect to the antifouling coating. Further experiments were performed in which the antifouling composition stated above was coated on a primer coating consisting of amide cured epoxy resin obtained by mixing Epon 1001 (Shell) and Versamide (registered Trade Mark) (General Mills), said primer coating being coated on substrates consisting of iron, aluminum, zinc, bronze and plastics (polyester), and the bonding and antifouling effect was good. The bonding of the antifouling composition to the substrate can also be improved by including per se well-known binders, such as those stated above. In further experiments the amide cured epoxy resin stated above was included in a quantity of 30 or 60 grams of the mixture of Epon 1001 and Versamid in the quantity of coating composition stated in the example above. Also this composition was tested on substrates consisting of iron, aluminum, zinc, bronze and plastics (polyester) with good effects.

In further experiments the coating was heated for sinter to substrates of iron, aluminum, bronze and zinc.

Essentially the same coating film thickness of about 5—10 microns in the dried state was used in all the examples stated above.

Further examples were conducted by adding 10% of glass beads with an average diameter of 5 microns or 30 microns in the coating composition.

The experiments stated above were repeated with Cu_2O substituted for half of, or the entire copper metal constituent.

Satisfactory results were obtained in all cases.

WHAT WE CLAIM IS:—

1. A ships bottom or other surface that requires protection against adherence of organisms that can grow on surfaces submerged in water, in which the surface carries an antifouling coating comprising a fluorocarbon polymer and an anti-fouling agent that can counteract growth of organisms on surfaces submerged in water.

2. A surface according to claim 1 in which the fluorocarbon polymer comprises polytetrafluoroethylene.

3. A surface according to either preceding claim in which the molecular weight of the fluorocarbon polymer is from 2000 to 5000.

4. A surface according to any preceding claim in which the anti-fouling agent is selected from tin compounds, arsenic compounds, mercury compounds, copper compounds, copper metal, solid chlorinated hydrocarbons and mixtures of two or more of these.

5. A surface according to claim 4 in which the coating comprises polytetrafluoroethylene together with copper powder and/or Cu_2O.

6. A surface according to any preceding claim in which the coating additionally comprises molybdenum disulphide and/or graphite.

7. A surface according to any preceding claim in which the coating contains 10 to 50% fluorocarbon polymer and 5 to 50% anti-fouling agent, the percentages being by weight based on the dry weight of the coating.

8. A surface according to any preceding claim in which the coating is 5 to 15 microns thick.

9. A surface according to any preceding claim in which the coating has been formed by applying to the surface a dispersion in a liquid dispersion medium of particles of the fluorocarbon polymer and the anti-fouling agent.

10. A surface according to claim 9 in which the dispersion medium includes a liquid halogenated hydrocarbon.

11. A surface according to claim 1 substantially as herein described.

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