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(54) A method of durably and lastingly protect a surface in contact with water from biological fouling

(57) An environmental friendly, long-lasting, practical, effective and economic method of rendering a surface antifouling properties is achieved by attaching a very thin copper-containing layer, sheet or foil directly to said surface so as to form an electrically conductive layer. These copper-containing sheets are, according to the invention, protected from oxidation by intermittently applying a cathodic protection.

First, copper has been believed to prevent biological growth as a result of the leaching of copper-ions. All previous methods, based on copper, have therefore been designed to release copper-ions, which pollutes the water and causes harm to the biological life. It was thus highly surprising that, by the application of intermittent cathodic protection to the copper-containing sheets, a method which essentially and totally prevents all release of copper to the aquatic environment, the antifouling properties were still maintained. As no corrosion occurs very thin layers can be used adding further advantages to the method such as ease of application, weight and cost.

Secondly, it was found, surprisingly and contrary to common belief, that such very thin layers in the form of copper-containing sheets, because of their low weight, flexibility and feeble thickness, could be made to follow any shape so closely, that many commercially available water-resistant adhesives are sufficient to exclude water from penetrating in-between the surface and the copper containing sheet so that said sheets are basically held in place by the hydraulic pressure exerted on the sheet, once the structure is submerged.

The new method avoids all the disadvantages of the more common use of toxic paints, as the surface will have a lower degree of roughness, be smear-free, offers long-term protection, eliminates the environmental hazards and further protects the surface from other effects of its contact with water.

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Description

Background of the Invention

[0001] The problem of preventing the biological growth on ships' hulls, so called fouling, is a serious one with a considerable economic impact. This growth of biological films, shells, algae and other species constitute a major drawback in as much as it adds significantly to the water resistance, reducing speed and adds to the overall costs of propagation. Unhindered growth may also lead to damage of the hull, causing pitting and corrosion.

[0002] Thus, over the years, several methods have been found to counteract this growth and effectively prevent it. Although effective these methods still prove insufficient with regards to durability and long time efficiency, environmental safety, health and security for the people carrying out the work of preparing the operation of protection as well as further aspects of overall economics.

Antifouling paints.

[0003] Today the most common method of antifouling constitutes of painting the hull with paint containing one or several toxic substances. Such toxic substances are typically based on copper, tin or more recently also biocides having a low solubility in water thus leaching only slowly. Substances of high toxicity have been used but their use has been shown to pose unacceptable environmental hazards and they have consequently been banned from use in many countries. Thus today practically all antifouling paints are based on copper-containing and copper-containing derivatives. The above mentioned high toxicity products had the advantage of being effective over a range of years whereas the copper-containing based paints in realty rapidly loose so much of its potency that a new layer of paint have to be applied mostly every year.

[0004] As the toxic pigments, flakes, particles or components are imbedded in a paint matrix, its rate of leaching is not constant. The layer exposed to the water is first exhausted, later followed by deeper laying layers. For this reason the antifouling paints becomes less and less effective with exposure time. This is particularly true for pleasure boats, many of which spend most of their time at rest at their moorings. Hence the antifouling is subdued to little attrition and the active antifouling components have to diffuse through the paint layer to reach the water.

[0005] To compensate for the loss of antifouling efficiency with time, the paint matrix is frequently made of components permitting the release of the toxic substance when in contact with water.

[0006] The matrix thus assumes an open structure actually absorbing the water and some types, so called self polishing, dissolves slowly I water. This inevitable and necessary property of constituting an open structure strongly reduces the paints protective qualities in all other respects than its antifouling properties. It is well known that such paints offer no protection against so-called "osmosis", the uptake of water by the polyester laminate, frequently being the preferred material for boat construction. The antifouling paints, equally, offers no or very poor additional protection of the hull against mechanical chocks.

[0007] Also, antifouling paints, because of its open structure, are mat, giving the underwater surface a rough finish. This roughness, which is in the order of 250 microns, adds significantly to the water resistance and the cost of propelling the vessels.

[0008] The work involved in repainting a ship or boat is a cumbersome one. First the boat or ship has to be docked or lifted out of water by means of a crane or similar device. Secondly, it has to be cleaned thoroughly. This is frequently done by high-pressure water jets or by brushing. Any residual shell or algae growth has to be removed separately or manually. After drying, a refurbishing of the primary layer of protective paint may be necessary followed by the application of one or several new coats of antifouling paint. The annual cost for this operation is considerable, with inconvenience and immobilisation of the vessel not be mentioned.

[0009] The use of antifouling paints is highly questionable also from another, environmental, point of view. As the hulls need to be repainted regularly, they have to be cleaned and rinsed prior to the application of a new coat of antifouling paint. Such cleaning is frequently performed with the boat standing on land. Pleasure boats, for instance, are assigned the same area for "winter" storage every year and its here that the cleaning takes place. It goes without saying that such an area becomes heavily polluted from the yearly accumulation of antifouling paint residues and that such a practice poses a potential risk to the surrounding environment and to the health of people staying there.

[0010] A further inconvenience with antifouling paints is its property to smear on contact. Whilst the boat in water, any contact with the antifouling paint will cause smearing of the object with the paint leaving patches that are difficult to remove. Many have had their ropes, fenders and bathing suits destroyed by contact with antifouling paint.

[0011] It is clear that a whole range of serious drawbacks and disadvantages accompanies the use of antifouling paint. Its abundant and common use is solely explained by the present lack of practical alternatives.

Other methods.

[0012] Before the evolution of shipbuilding permitting to use materials like steel, aluminium or various plastics, hulls were made of wood. The underwater parts were protected by covering the hull beneath the water line by nailing sheets of copper by the use of copper nails to the wooden hull.

[0013] Experience using steel nails rapidly proved fatale as the steel nails corroded away within short and the sheets ran the risk of falling off. The copper-containing plates were thick, to be able to be handled and hence heavy. However, the antifouling effect was quite satisfactory and lasted many years although its efficiency diminished with time as a result of the formation of copper oxides on the surface.

[0014] With the arrival of steel hulls the use of copper-containing plates became impracticable, as no reliable and yet sufficiently uncomplicated way of attaching the plates to the hull had been developed. As late as in the 1980es, though, full-scale tests were made using a welding technique, which is reported to have been successful. (Review of Copper-containing-Nickel Alloy Sheathing of Ship Hulls and Offshore Structures, Dale T. Peters, Copper-containing Development Association). No fouling could be detected after several years of use and the plates had only lost about 10 microns of its thickness per year in spite of its exposure to the high speeds and prolonged harsh conditions accompanied with the activities of commercial vessels.

[0015] Thus, the use of copper-containing plates is known to constitute an efficient way of protecting underwater surfaces against fouling. Until now, however, its use has been hampered by the lack of methods of bonding the copper-containing plates to the surfaces.

[0016] Yet, some attempts have been reported to enable the bonding of copper-containing plates to the underwater parts. These reported methods all include the prior bonding of the copper-containing plates to some supporting sheet or layer.

[0017] Two Japanese patents (EP0562441 and EP0562442) describe a way of using copper or copper beryllium sheets as antifouling primarily for tubes. The patents claim that the use necessitates the attachment of an "insulating layer" to the copper sheets. The composite nature of this product hampers its application on complicated shapes like boot hulls. No reference was given to the thickness of the sheets, nor to the nature of the bonding.

[0018] The US patent US4987036 describes a method trying to overcome the problem of using copper-containing sheets to surfaces for their protection against fouling. Also this method necessitates the prior bonding of the copper-containing sheets to a supporting structure, made of a mesh, grid or an elastic material, for subsequent bonding of this laminate, using exclusively a curable neoprene rubber, to the surface to be protected. This method overcomes the problem of covering curved shapes by first bonding, to the above mentioned supporting structure, narrow copper or copper nickel sheets comprising a plurality of individual strips of copper or a copper-nickel alloy in the form of substantially parallelogram in shape.

[0019] It appears that the problem, which has not yet been overcome, is the direct bonding of copper-containing sheets to surfaces exposed to water and fouling conditions, such as ship or boat hulls. To add to the problem, copper is a rather heavy metal with a density of 8.4 kg/l. A plate of 4 mm thickness, which was often used during the above-mentioned full-scale tests, thus weighs a full 33.6 kg/m2. This considerable weight adds to the complications of assuring a firm bonding of the copper-containing sheet to the surface to be sheeted. The use of epoxy or polyurethane patty also proved unsatisfactory in the above-mentioned study (Review of Copper-containing-Nickel Alloy Sheathing of Ship Hulls and Offshore Structures, Dale T. Peters, Copper-containing Development Association).

[0020] Another factor that may have hampered the use of copper sheets is the subsequent loss of effectiveness after some time of use. Copper gets oxidised and as this copper oxide layer gets thicker it appears to loose its antifouling effect. Although this loss in effectiveness usually becomes apparent only after some years of use the old practice was nevertheless to give the copper plates a treatment of abrasion or slightly grinding it so as to remove this oxidised layer.

[0021] Thus until now, in spite of the colossal economic impact such a practice would have, no method has been presented permitting the effective or commercial use of copper-containing sheets for antifouling purposes for complicatedly shaped surfaces like ship or boat hulls.

Environmental considerations

[0022] Great concern has recently been raised regarding the environmental impact of the use of toxic antifouling paints. High concentrations of ions of the metals, mostly tin and copper, used in those paints have been measured in harbours and mooring waters. It appears that the antifouling paints release their content of toxic substances in an uncontrolled way leading to mentioned high concentrations. These metal ions have been shown to be absorbed by organisms having a detrimental effect on their ability to proliferate.

[0023] Particularly worrisome is the fact that antifouling paint releases most of its toxic substances during the first few weeks the boat is launched into water. This is usually in the springtime when water organisms are in a delicate phase of their lifecycle. Due to the cold water, first there are very few of them and secondly they form extremely little fouling during these spring weeks.

[0024] Actually no antifouling would indeed be needed at all during this early period. And during this time the paints release high amounts of toxic substances. This is a most unsatisfactory state of affair indeed.

[0025] The problem has been recognised by the authorities in many countries and regulations have been imposed on the release rate of such metals from antifouling paints. Thus, as an example, many countries in the European Union has introduced a ban on all tin containing paints for pleasure boats, although commercial craft may continue to use such paints where however the release rate must not exceed certain levels.

[0026] Also paints containing copper have been regulated in some countries. In Sweden for exempel, such paints are not allowed to release more than 200 micrograms of copper per cm2 during the first 14 days in contact with water as measured by a standardised analytical method. Also other countries have introduced such restrictions.

[0027] It is interesting to note that the existing antifouling methods in fact do not take into account at all when they are actually needed.

[0028] For instance, all during the winter period or in cold waters no or virtually no antifouling is required at all. Equally, it is generally established that when a hull is moving trough water at speed over 2m/sec the biological species fail to adhere to the hull because of the high velocity gradients.

[0029] Also, most algae depend on light for their metabolism so that during the night no antifouling is needed either.

[0030] On top of all this the existing toxic antifouling methods release lethal doses of toxic metal ions in spite of the simple fact that the micro-organisms need not be killed at all. Of relevance are only those organisms that actually cause an increased water resistance for the hull as it moves through water. Such organisms are seaweed, barnacles and various mussels, for example. They all have in common to attach to underwater surfaces by means of special organelles excreting specific proteins (rich in the aminoacid DOPA) which are covalently bonded to the surfaces on the action of an enzyme complex, which for some species have been isolated as a catechol oxidase system. These enzymes are denatured by heavy metal ions like tin, mercury, cadmium and also by slightly higher levels of copper although some copper must be present for the enzyme to function.

[0031] An efficient antifouling thus only needs to act on the actual attachment phase by blocking these enzyme systems. Indeed the biochemical reactions leading to fouling takes place in the very vicinity of the surfaces, probably within a few microns. An antifouling thus has to be active only in this extremely thin layer thus blocking the adherence of the organisms to the hull.

[0032] Moreover, organisms attachment and growth on surfaces is a slow process. It takes several days or weeks for these species to grow in size to the extent that their shape may cause additional drag to a hull. It thus seem completely unnecessary to release toxic substances continuously when intermittent protection depending on circumstances would be more than appropriate.

[0033] In fact, it has until now been generally agreed that copper antifouling is effective as a result of the release of copper ions. However, the present invention completely contradicts this general belief in so far as antifouling was achieved without any measurable loss of copper from the copper-containing layers or sheets.

Description of the invention.

[0034] The present invention describes a method, a product and its application, permitting an effective and practical use of copper-containing conductive layers to counteract biological fouling on any surface including complicatedly shaped surfaces such as boat-or ship hulls in particular.

[0035] The new method completely eliminates the detrimental effect on the environment normally resulting from antifouling active substances.

[0036] The method offers a breakthrough in the way the antifouling effect can be controlled as the effect can be "switched" on and off in line with the need for antifouling.

[0037] The copper-containing conductive layer may be constituted of plates, sheets, foils, grid or mesh or smaller pieces such as flakes of such applied so as to form a conductive layer.

[0038] The method moreover overcomes the difficulties of bonding copper-containing sheets to surfaces, curved in three dimensions.

[0039] The method also and additionally provides further protection of the underwater surfaces against damages caused by the surfaces contact with water such as so called osmosis and the method adds to the strength of the structure and its resistance to mechanical shock.

[0040] The use of the method further reduces the roughness of the hulls thus permitting improved fuel economy or higher speeds.

[0041] The protected surface, moreover, becomes essentially smear-free thus offering enormous advantages both when it comes to handling of the protected surface and the almost total absence of environmental impact when cleaning.

[0042] The method provides protection from fouling over a period of several years.

[0043] In fact the solution to the previously described problems of sheathing is the following:

[0044] By protecting the copper from corrosion the use of very soft and very thin copper-containing sheets may be used. Yet thick enough to last several years under harsh marine conditions and to give long-term protection against fouling, these sheets can successfully be shaped and bonded to any surface without the use of welding, fasteners like nails or prior bonding to insulating layers, supporting films or structures. Equally, the use of such thin sheets avoids the otherwise necessary use of narrow strips to cover complicated shapes.

[0045] As thin copper-containing sheets are light-weight its bonding to the surfaces to be protected becomes much less complicated. Such thin sheets are basically held in place by the action of the hydraulic pressure exerted on it by the water, provided that no water is allowed to trickle in between the sheets and the hull. In fact this surprisingly simple idea permit the use of most commercially available water resistant adhesives suitable for the bonding of copper-containing onto the surface in question to be protected. These copper-containing sheets are so lightweight that the pressure exerted by the depth of water helps to keep them in place, easing the strain on the bonding adhesive.

[0046] The problem of loss of efficiency over the years as a result of the formation of an oxidised layer is also overcome by the use of anticorrosion measures. By rendering the copper surface cathodic no oxidation can take place and the surface remains in its copper metal state. Such methods are in common use to protect principally steel constructions from corrosion and are known as "cathodic protection". Such cathodic protection can be achieved either by assuring a metallic contact between the metal to be protected and a so called sacrifice anode, made by a less noble metal, mostly zinc or aluminium, or by applying a source of electricity in the form of a direct current thus rendering the surface to be protected passivated or immunised.

[0047] Attempts have been reported to counteract the corrosion of copper in seawater by using such cathodic protection but they were quickly abandoned as it was noted that the antifouling effect disappeared.

[0048] In this invention, such cathodic protection is nevertheless employed as it was surprisingly observed that removing the cathodic protection for short periods of time restored the antifouling effect without loosing any of the protection regarding corrosion. This particularly interesting aspect of the invention offers a completely unique and novel method to prevent fouling without any environmental impact whatsoever.

Detailed description of the invention.

[0049] It was felt that not enough consideration had been taken to ensure a practical use of copper-containing sheets for boat-or ship coating. Thus a copper-containing sheet must be so soft as to be able to follow the geometry of the surface to be sheeted regardless of its shape. Hence a very thin sheet or foil indeed should be used. To ensure a permanent bonding to the surface to be sheeted, it must in fact be so soft as to form essentially watertight agglomerate with the surface so that no or very little water may trickle in between the copper-containing sheet and the surface.

[0050] Copper-containing materials are heavy and thick plates may not become sufficiently bonded to withstand its tendency to fall down by its own weight. Also this is avoided using very thin sheets or foils. Such thin sheets may basically be held in place by the hydrostatic pressure exerted on them by the water pressure, provided that essentially no water is permitted to enter between the surface to be protected and the copper-containing sheet itself. Such close contact can be achieved by the use of one or several commercially available adhesives.

[0051] However, copper containing sheets not protected against corrosion must not be too thin. They should, of course, be sufficiently thick so as not to corrode away too quickly, making the use impractical. As it has been reported that, under realistic conditions on commercial vessels, the rate of corrosion is in the order of 10 microns per year, the practical absolute minimum thickness would thus be some 50 microns.

[0052] The copper-containing sheet must additionally have properties such as to permit its firm bonding to the surface to be sheeted. Also this is facilitated by the use of very thin and soft sheets.

[0053] Copper-containing materials have a high thermal expansion coefficient, which differs much from that of the materials normally used for ship-and boat hulls. A thin and soft copper-containing sheet exerts less global strain on the bonding than a thick one as the temperature changes.

[0054] Likewise, which has been totally neglected in previous attempts, the surface to be coated must also be prepared so as to enable its sheathing. Also this aspect is covered by the new invention.

[0055] Finally, to be practical, the sheathing must be reversible, i.e. some day, eventually, all hulls must be refurbished and the removal of the sheathing must not be virtually impossible, risk to destroy the hull itself or otherwise cause damage to it. One aspect of the new invention takes full account of this most important aspect.

[0056] In one aspect of the present invention, thin, soft copper-containing sheet or foil is bonded directly, without the need for supporting films or structures, to the curved surfaces to be protected by the use of any commercially available adhesive suitable for the water resistant bonding of copper-containing onto the surface to be protected. Because of the softness and the low weight of such thin copper-containing foils the strain on the bonding is low and the bonding itself, with the proper selection of adhesive, becomes stronger than the foil itself. The practical thickness of the foils was found to be in the range of 10 to 250 microns.

[0057] In a further aspect of the invention, thin copper-containing sheets or foils can be prepared in advance with a water-resistant adhesive, which can be activated at a later time when the actual sheathing is to take place. Such adhesives can be any of the types found among the group of "tapes", known under the commercial names as "Scotch", "Tesa" etc. Such adhesives are frequently derivatives of acrylics but the invention is in no way limited to the use of such acrylics as any water-resistant adhesive can be used. The foils may thus be prepared in advance to form a composite tape where the adhesive side would be covered by a so-called release cover to be removed just prior to the sheathing. Also other suitable adhesives can be used as those activated by heat, solvents or other methods.

[0058] In yet another aspect of the invention, thin copper-containing sheets can be used to constitute an integral part of a ship's or boat's hull. Boats made of glass fibre reinforced resins, like polyester, epoxy etc. are produced by laminating the fibreglass with the resin in moulds. When the laminate has hardened and cured, the mould is removed and the hull is then fitted with such further details as to make it complete. The bottom must then be painted with antifouling.

[0059] However, the present invention facilitates the completion of the hulls. In this aspect of the invention, the copper-containing sheet is first placed on the part later of the mould later to hold the underwater part of the hull, then the laminating proceeds as usual, taking into full account to use a laminating resin having a sufficient adhesion to the copper-containing foil. When the laminate has hardened and cured and the mould has been removed, the hull already has its underwater part sheathed with the copper-containing sheet. In this way the finished hull will have an incorporated antifouling treatment. The same technique can be used for any item, produced in moulds and which should possess antifouling properties

[0060] In one especially efficient aspect of the invention, the copper-containing sheets are mounted to the surface in such a way as not to expose any edge of copper-containing sheet to the main direction of the water flow. This may be achieved by ensuring to overlap the sheets "downstream" thus effectively reducing the risk of the sheets being peeled off by the action of the flow of water over the surface when the vessel is making headway.

[0061] A breakthrough in antifouling technique is offered in the aspect of the invention where the antifouling effect can be controlled as to coincide with the need to prevent fouling. Copper metals in contact with natural water having slightly basic pH values may exist in three distinct states: At a low enough redox potential copper shows immunity and no corrosion occurs.

[0062] Secondly, at higher redox potentials, copper can also be in a passive state which is also corrosion free but an oxidation to $Cu2O$ or CuO occurs on the surface. Thirdly, full corrosion occurs at high redox potentials, low or high pH values and in the presence of anions like chloride. Copper is in this state released as Cu 2+ or $CuO2$ 2- ions. Which state copper is in is thus a function of its redox potential. Copper in its immune state is inert and does not corrode which is favourable but on the other hand does not offer any antifouling properties either. The passive phase or state is antifouling active but a layer of copper oxides develops, grow thicker and the antifouling diminishes with time. This invention relates to alternating between these states.

[0063] The transition from immune to passive and visa versa can be controlled. Such a controlled effect can be established by the connection of an sacrifice anode, made of a metal less noble than copper, to the copper containing sheet in such a way that said connection may be disconnected at intervals. As an example the anode may be connected to the copper sheets by means of a circuit via a switch, which can be closed or opened. When the switch is open the anode is not electrically in contact with the copper-containing conductive layer or sheet and thus the copper is in an active phase as to what corrosion concerns. However, when the switch is closed, the anode is again connected to the copper sheet and the cathodic protection is restored. Said switch may be operated by a timer or other device so as to regulate the time intervals. The same effect can be achieved by mechanical means, making the anode alternating between being physically in contact with the copper sheet and not in contact. A third possibility is to use an applied current from a separate current source.

[0064] This particularly effective method ensures that the copper containing sheathing remains antifouling-effective as no oxide layer develops and on the same time the copper surface is fully protected from corrosion.

Example 1.

[0065] A piece of copper foil, 100 micrometers thick, was weighed accurately, connected with a cable via a timer-controlled switch to an aluminium rod and the copper and the rod were subsequently immerged in seawater maintained at approximately 20 deg C with a salt content of 3%. The timer was set to close the circuit for 45 minutes and disconnect the aluminium anode from the copper sheet for 15 minutes, this cycle repeating every hour. The copper sheet was weighed at intervals and the biological growth observed.

[0066] The result was very surprising.

[0067] No corrosion at all could be detected as the copper remained oxide free but lost no weight. No fouling occurred either even after four months exposure, showing that the surface remained nevertheless active in protecting against fouling.

[0068] A control piece of inert Teflon was covered by a thick layer of algae. Another control piece of copper foil without any cathodic protection was equally covered by a layer of algae. The table below shows the test results.

Days	Loss (Calculated as µm/year from start of test)
4	1.8
8	-6.7
14	-6.7
27	0.1
59	0.1

[0069] As can be seen no weight loss calculated as loss in thickness per year due to corrosion could be noticed during a 60 days of trial. The irregularity and the negative signs were due to some accumulation of mineral particles on the copper sheet which was not cleaned until on the 59th day so as to permit an inspection of possible biological fouling.

Example 2.

[0070] It was surprisingly found that copper-containing foil as thick as typically 100 micron of the soft quality, supplied by the company Outokompu, Västeras, Sweden could be shaped to follow any curvature present on boat hulls. This thickness would correspond to about ten years of heavy use, a considerable advantage compared to antifouling paint practice of repainting mostly every year. The roughness of the copper-containing foil was in the order of 5 microns.

[0071] It was also surprisingly found that this relatively thin foil, after having been cleaned from grease, loose oxides and dust, permitted a strong adherence to surfaces using simple "neophrene contact" glue", commercially available from the companies 3M, Henkel and others.

[0072] Thus a surface (in the form of a centreboard keel) was sheathed using the above-mentioned method. To ensure an optimal adherence, the surface to be protected was prior to the sheathing painted using a two component polyurethane paint. Several such paints are commercially available. It was not considered vital to use polyurethane paints and any water-resistant paint giving a reasonably even and smooth surface would give the same result.

[0073] Surfaces so prepared were subdued to severe testing including twenty cycles of consecutive freezing and prolonged, 48 hours, exposure to 40 °C warm salt-water. The surface was equally subjected to 80 bar water jet cleaning. Neither of these conditions led to any visual separation of the copper-containing foil from the surface.

[0074] Then the surface was mounted under water on a boat in order to evaluate its properties under real conditions. After one full year of service no sign of release or separation was to be detected and the surface remained essentially free of fouling.

Example 3.

[0075] It was even more surprising to find that, using such copper containing foil as in example 1, even so called "sticking tape" (known commercially as Scotch, Tesa etc.) provided sufficiently strong bonding.

[0076] The surface to be protected was first prepared in the same way as in example 1 but using a glossy paint.

[0077] Normally boat and ship hulls are painted on their underwater parts using mat primer paints, which offers a better base for the subsequent application of antifouling paints. However, it was found that copper-containing sticking tape adhered just as well to glossy paint.

[0078] As the paint had cured, the surface of the hull to be studied was first clad with the double-sided tape (so called adhesive transfer tape available from the company 3M) making sure to cover the entire underwater surface and a band some decimetres above the waterline. The protective film facing the outside was left in place.

[0079] Then after successive removal of the protective film, the copper-containing-containing foil was pressed firmly, against the adhesive tape by the aid of a rubber roller. Care was taken not to enclose any air under the copper-containing-containing foil. Thus the work proceeded until the entire surface, to be studied, was covered. Although glossy paint was used in this example, the invention is in no way limited to the use such paint as also mat paint gives satisfactory results.

[0080] The fact of using a sub millimetre sheet, which was not heavy, made the work possible giving a most satisfactory result essentially without wrinkles. In fact, a ship or boat hull must be very smooth and even so as to exert the minimum of resistance when the ship makes way.

[0081] The boat was then launched.

[0082] The water exerts a hydrostatic pressure (depending on the depth beneath the water surface) on the hull. As the copper-containing-containing sheathing was so thin and the fact that its weight was only 0.84 kg per m2 the hydrostatic pressure actually counteracted the weight of the copper-containing sheathing so that in theory no further bonding would be required under static conditions, which explains why such a relatively unqualified adhesive turned out to have sufficient bonding strength. However, a boat or ship does not stay at rest and the water swirling by, when the hull makes headway, exerts a force on the sheathing. To avoid "peeling" off of the sheathing, it was applied in such a way as to ensure that all overlapping of the sheets was done "downstream" i.e. the surface was clad from stern to bow.

[0083] In one case, a band of such metal tape remained firmly attached to the boat hull after 17 full years!

[0084] It thus appears to be much less complicated than generally thought to adequately bond copper-containing-containing sheets to a boat or ship hull.

[0085] The copper-containing-containing sheet could be easily removed by heating the sheet by means of a hot air gun and a scraper.

Example 4.

[0086] As in example 1, the surface to be sheeted was first prepared by proper cleaning, sanding and painting with a polyurethane paint.

[0087] Separately, a copper-containing sheet, 100 microns thick and from the same supplier, had been washed and treated to ensure the removal of grease and loose oxides. After drying, the double-sided transfer tape was applied to the copper-containing sheet, leaving the protective outer film intact.

[0088] The protective film was then removed and the copper-containing sheet, with its transfer tape, was pressed against the surface of the boat hull by means of a rubber roller.

[0089] Also this procedure gave a most satisfactory result.

Example 5.

[0090] The surface to be protected was prepared in the same way as in example 1, 2 and 3. The surface was then coated with a heat sensitive adhesive tape, available from 3M Company. Such tapes perform like ordinary tapes but their bonding properties can be much improved on heating the substrate after the initial bonding. Thus the copper-containing sheet was applied in the same way as in example 1 and 2 but the surface was later heated using an electrically heated "iron" device so as to cure the bonding according to 3M's specifications.

[0091] This treatment resulted in an equally solid bonding. Subsequent attempts to remove the sheathing, with the aim of simulating a major overhaul, proved difficult, as the bonding was very firm indeed. New sheathing could therefore be made on top of the existing one.

Example 6.

[0092] A mould, normally used for the production of boat structures, was first clad with the thin copper foil on the part to be under water in the finished hull. Then, on top of the copper foil, this area was laminated using epoxy resin and a thick glass fibre weave, commercially readily available.

[0093] The lamination then preceded using resin and fibreglass in the usual manner until the part was finished. After release from the mould, the part of the structure, to be submerged, was thus sheathed with the copper foil.

Claims

1. A method of durably and lastingly protect a surface in contact with water from biological fouling and on the same time protecting it from other effects associated with its contact with water by the application onto the surface of a thin electrically conductive copper-containing layer or sheet, permitting a water-proof and close bonding to curved surfaces, forming an essentially homogeneous surface composite, essentially free from cavities, characterised in that the copper-containing layer, sheet or foil is protected against oxidation and corrosion using an cathodic protection which is alternately switched on and off at time intervals, the frequency of which might be varied depending on aqueous environment.

2. A method according to the preceding claim characterised In that the cathodic protection is achieved by assuring a metallic contact between an anode made from a metal different than copper, and the copper-containing layer, sheet or foil.

3. A method according to the preceding claim characterised in that the metal used for making the anode is preferably zinc or aluminium.

4. A method according to claim 1, characterised in that the cathodic protection is achieved by applying to the copper containing layer, sheet or foil a source of electricity in the form of a current rendering the surface to be protected immunised.

5. A method according to any of the preceding characterised in that an electrical circuit including a switch is interconnected between the copper-containing sheet or foil and either the anode or the direct current source.

6. A method according to the preceding claim, characterised in that the switch is operated by a timer regulating the time intervals.

7. A method according to claim 5, characterised in that the switch is activated by at least one sensor regulating the time intervals depending on predetermined conditions.

8. A method according to any of the claims 2 and 3, characterised in that mechanical means are inserted between the anode and the copper-containing layer, sheet or foil, making the anode alternating between being physically in contact with the said copper-containing layer, sheet or foil and being out of contact with the latter.

9. A method according to any of the preceding claims, characterised in that the thickness of said copper-containing layer, sheet or foil is less then 0,2 mm, preferably between 10 and 100 microns.

10. A method according to the preceding claim characterised in that said thin copper-containing layer, sheet or foil is held in place by basically the hydraulic water-pressure exerted on any submerged surface and is applied to the surface by a suitable adhesive means able to exclude penetration or trickle of water between the surface to be protected and the copper-containing sheet thus maintaining the hydraulic pressure on the surface, and excluding any cavities or channels permitting the water to trickle in between the sheets and the surface to be protected from fouling and other effects of its contact with water.

11. A method according to any of the claims 1 to 9, characterised in that the surface is sheathed with said copper-containing sheet or by placing the sheet or foil in a mould, to be later included in a resin laminate with its cuprous side facing the side intended to be exposed to the water.

12. Application of the method of the preceding claims to the protection of ship's bulls.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 00 44 0142

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	EP 0 364 630 A (ANDOE GRAHAM C) 25 April 1990 (1990-04-25) * page 5, line 8; claims 1,8 * ---	1-3	B63B59/04 C23F13/00
X	EP 0 550 766 A (NAKAGAWA CORROSION PROTECT) 14 July 1993 (1993-07-14) * claim 1 * ---	1	
A	WO 99 43618 A (MATSUNAGA TADASHI ;MURAKAMI NOBUYUKI (JP); NAKAMURA NORIYUKI (JP);) 2 September 1999 (1999-09-02) * abstract * & EP 0 985 639 A (MATSUNAGA TADASHI) 15 March 2000 (2000-03-15) ---	1	
A	EP 0 468 739 A (DAIKI ENGINEERING CO) 29 January 1992 (1992-01-29) * claim 1 * ---	1	
A	FR 2 256 072 A (ZONDEK KLAUS) 25 July 1975 (1975-07-25) * the whole document * -----	1	

TECHNICAL FIELDS SEARCHED (Int.Cl.7)

B63B
C09D
C23F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 October 2000	Zaegel, B

CATEGORY OF CITED DOCUMENTS

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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 00 44 0142

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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26-10-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0364630 A	25-04-1990	US 4772344 A	20-09-1988
		AU 619484 B	30-01-1992
		AU 2219888 A	22-03-1990
		GB 2222832 A,B	21-03-1990
EP 0550766 A	14-07-1993	AU 651491 B	21-07-1994
		AU 2346092 A	23-02-1993
		CA 2092304 A,C	25-01-1993
		WO 9302254 A	04-02-1993
		JP 3061860 B	10-07-2000
		KR 187600 B	01-06-1999
		US 5344531 A	06-09-1994
WO 9943618 A	02-09-1999	JP 11244861 A	14-09-1999
		JP 11264062 A	28-09-1999
		JP 11309459 A	09-11-1999
		JP 11333465 A	07-12-1999
		JP 2000008338 A	11-01-2000
		EP 0985639 A	15-03-2000
		EP 0961186 A	01-12-1999
EP 0468739 A	29-01-1992	JP 2045707 C	25-04-1996
		JP 4078482 A	12-03-1992
		JP 7024822 B	22-03-1995
		DE 69108630 D	11-05-1995
		DE 69108630 T	04-01-1996
		US 5182007 A	26-01-1993
FR 2256072 A	25-07-1975	NONE	

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82