[0006] WO-2007/088172 discloses compositions containing tralopyril and a broad range of zinc compounds such as e.g. ZnO, $ZnCl_2$, $ZnSO_4$, zineb and zinc pyrithione having a synergistic antifouling effect.

[0007] The wording "essentially free of cuprous oxide" as used herein means that the compositions of the present invention do no comprise cuprous oxide that has been intentionally added to the compositions.

[0008] Surfaces or objects exposed to humid or aqueous environments are readily colonized by aquatic organisms such as algae, fungi, bacteria, microbes, and aquatic animals such as, e.g. tunicates, hydroids, bivalve mollusks, bryozoans, polychaete worms, sponges and barnacles. As these organisms settle on or attach to said surfaces, the value of the exposed objects diminishes. The attachment or settlement of said organisms is also known as 'fouling' of a structure. The exterior, but possibly also the interior of the object may deteriorate, the surface changes, e.g. from smooth, clean and streamlined to rough, foul and turbulent, the weight of the object increases by the deposit of the organisms and their remnants, and the vicinity of the object may become obstructed or encumbered. The function of the object and system involved lowers and the quality of the aqueous environment deteriorates. The common method of controlling the attachment of fouling organisms is by treating the structure to be protected with a coating which comprises an antifouling agent.

[0009] The combinations of antifouling biocidal compounds as claimed in the present invention are especially suitable to protect surfaces or objects in constant or frequent contact with water from fouling or attachment or settlement of algae, by applying to said surfaces or objects a composition comprising component (I) and one of the components (II) in respective proportions to provide a synergistic effect against fouling organisms. Alternatively, combinations of component (I) and one of the components (II) may be incorporated into the substrate to be protected from fouling. In a first aspect, there is provided a composition comprising a combination of a component (I) and a component (II) in respective proportions to provide a synergistic effect against fouling organisms, whereby component (I) is selected from ferric benzoate (I-a), aluminium benzoate (I-c), barium benzoate (I-d) and calcium benzoate (I-e), and tralopyril as component (II); with the proviso that said composition is essentially free of cuprous oxide.

[0010] Examples of said surfaces or objects are for instance, flexible nets or rigid cages used in marine or freshwater aquaculture, fishing nets, ship hulls, harbor installations, piers and pilings, drying docks, sluice-gates, locks, mooring masts, buoys, offshore oil rigging equipment, drilling platforms, bridges, pipelines, cables, ballast water tanks, ship reservoirs that draw water from infested bodies of water, recreational equipment, such as surfboards, jet skis, and water skis, and any other object in constant or frequent contact with water.

[0011] The disclosure~~invention~~ also provides a method to protect materials, in particular surfaces or objects in frequent or constant contact with water, against fouling organisms by applying to said objects a composition comprising an effective antifouling amount of a combination of a component (I) together with a component (II) wherein the amount of component (I) and component (II) are in respective proportions to provide a synergistic effect against fouling organisms.

[0012] The present disclosure~~invention~~ further provides a method of protecting a surface which comprises applying to the surface a composition comprising an effective antifouling amount of a combination of a component (I) together with a component (II) wherein the amount of component (I) and component (II) are in respective proportions to provide a synergistic effect against fouling organisms.

[0012a] In a second aspect, there is provided the use of a composition as defined above for the control of fouling organisms.

[0012b] In a third aspect, there is provided a method of protecting materials against fouling organisms, wherein the said method comprises administration or application of an antifouling effective amount of a composition as defined above.

[0013] An especially important use of the method of the disclosure~~invention~~ comprises a method for inhibiting fouling of nets used in aquaculture, which comprises applying to the net an antifouling composition in accordance with the invention. The effects of biofouling to the aquaculturist are largely detrimental. Hydrodynamic forces on a fouled net, which can reduce cage volume, constrict net openings and stress moorings, have been calculated at up to 12.5 times that of a clean net. Concurrently, the weight of cages can severely increase, causing further structural stress as well as a reduction in cage buoyancy and increased net deformation. Fouling can also cause physical damage to the nets themselves. Fouling effectively decreases the specified mesh size by increasing net surface area, which causes disruption to water flow. As a result, nutrient exchange and waste removal are restricted, which not only affects the health of stock but also the surrounding environment; for example, by causing localised eutrophication. Similarly, supplies of oxygen may be disrupted and anoxic conditions can develop; this is particularly pertinent in temperate regions during the summer when the period of most aggressive fouling coincideswith highwater temperatures that further reduce oxygen levels. Decreases in DO levels can be further compounded by the respiratory activity of fouling organisms themselves. Indirect effects of biofouling development on fish cages and netting include remedial costs; for example, cleaning and repairs which, in turn, have detrimental environmental implications and can further stress stock through increased disturbance. The complex fouling communities that can develop may indirectly cause further stress to stock by affording habitat to a range of 'harmful' diseases and parasites; for example, 'netpen liver disease', amoebic gill disease, the nematode Hysterothylacium aduncum and the sea louse Lepeophtheirus

salmonis. Fouling can also create 'Health and Safety' concerns, *i.e.* fouling increases the weight and slipperiness of equipment that is handled and, in the tropics, the frequency of contact with stinging and cutting organisms is raised. The increase in disease and parasites due to the development of fouling adds to the concerns over the use of combatant chemicals, such as cypermethrin, azamethiphos and emamectin benzoate, which are used for their treatment but have, potentially, detrimental environmental impacts. Despite the use of some preventative practical procedures, the main protective method against fouling, whether it be for ships or nets, involves the use of antifouling paints. These are applied to nets typically made from synthetic fibres, including polyamide (nylon). Antifouling paints containing only copper, in the monovalent form of cuprous oxide, is the paint technology used almost exclusively in the fish farming industry today. Antifouling paints based on cuprous oxide have a limited lifetime. Furthermore such coatings are known sources of pollution from aquaculture and are responsible for elevated levels of copper close to fish-farms. Net washing plants have problems dealing with the copper containing waste and sludge. The waste must be specially disposed of and such safeguards evidently increase costs.

[0014] Another important use of the method of the disclosure~~invention~~ comprises a method for inhibiting fouling of a ship's hull, which comprises applying to the hull an antifouling composition in accordance with the disclosure~~invention~~. Fouling on the hulls of ships for example increases frictional drag with a corresponding decrease in speed and maneuverability and an increase in fuel consumption and increased maintenance costs associated with removal of the fouling.

[0015] The compositions comprising a combination of a component (I) together with a component (II) wherein the amount of component (I) and component (II) are in respective proportions to provide a synergistic effect against fouling organisms can be used to protect constructions such as, e.g. swimming pools, baths, cooling water circulation circuits and industrial baths in various installations, e.g. in manufacturing plants or in air-conditioning installations, the function of which can be impaired by the presence and/or the multiplication of fouling organisms. Further examples are buildings and parts of buildings such as floors, outer and inner walls or ceilings, or places suffering from dampness such as cellars, bathrooms, kitchens, washing houses and the like, and which are hot-beds for fouling. Fouling not only is problematic from the viewpoint of hygiene and aesthetics, but also causes economic losses because said buildings and/or decorating materials deteriorate more rapidly than desired.

[0016] Another application of the combinations of the present disclosure~~invention~~ is the treatment or disinfection of ballast water to reduce or eliminate the presence of aquatic organisms such as phytoplankton (dinoflagellates and diatoms), crustaceans (crabs, shrimp, copepods, amphipods), rotifers, polychaetes, molluscs, fish, echinoderms, ctenophores, and coelenterates.

[0017] The synergistic antifouling compositions of the present disclosure~~invention~~ can also be used in a variety of applications :

- industrial aqueous process fluids, e.g. cooling waters, pulp and paper mill process waters and suspensions, secondary oil recovery systems, spinning fluids, metal working fluids, and the like
- in-tank/in-can protection of aqueous functional fluids, e.g. polymer emulsions, water based paints and adhesives, glues, starch slurries, thickener solutions, gelatin, wax emulsions, inks, polishes, pigment and mineral slurries, rubber latexes, concrete additives, drilling mud's, toiletries, aqueous cosmetic formulations, pharmaceutical formulations, and the like.

[0017a] In a fourth aspect, there is provided a product containing (a) a composition comprising a component (I) selected from ferric benzoate (I-a), aluminium benzoate (I-c), barium benzoate (I-d) and calcium benzoate (I-e); and (b) a composition comprising tralopyril as a component (II); as a combination for simultaneous or sequential use, wherein said (a) and (b) are in respective proportions to provide a synergistic effect against fouling organisms; with the proviso that said product is essentially free of cuprous oxide.

[0018] The term "fouling organisms" is meant to comprise organisms that attach, settle, grow on or adhere to various kinds of surfaces, in particular in humid or aqueous environments such as, marine waters, fresh waters, brackish waters, rain water, and also cooling water, drainage water, waste water and sewage. Fouling organisms are Algae such as, for example, Microalgae, e.g. *Amphora, Achnanthes, Navicula, Amphiprora, Melosira, Cocconeis, Chlamydomonas, Chlorella, Ulothrix, Anabaena, Phaeodactylum, Porphyridium;* Macroalgae, e.g. *Enteromorpha, Cladophora, Ectocarpus, Acrochaetium, Ceramium, Polysiphonia* and *Hormidium sp.*; fungi; microbes; tunicates, including members of the class Ascidiacea such as *Ciona intestinalis, Diplosoma listerianium*, and *Botryllus schlosseri*; members of the class Hydrozoa, including *Clava squamata*, *Hydractinia echinata*, *Obelia geniculata* and *Tubularia larynx*; bivalves, including *Mytilus edulis*, *Crassostrea virginica*, *Ostrea edulis*, *Ostrea chilensia*, *Dreissena polymorpha* (zebra mussels) and *Lasaea rubra*; bryozoans, including *Electra pilosa*, *Bugula neritina*, and *Bowerbankia gracilis*; polychaete worms, including *Hydroides norvegica*; sponges; and members of the class Crustacea, including *Artemia*, and Cirripedia (barnacles), such as *Balanus amphitrite*, *Lepas anatifera*, *Balanus balanus*, *Balanus balanoides*, *Balanus hameri*, *Balanus crenatus*, *Balanus improvisus*, *Balanus galeatus*, and *Balanus eburneus*; and *Elminius modestus*, and *Verruca*.