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UNITED STATES PATENT OFFICE.

GEORGE D. COLEMAN, DECEASED, LATE OF BUFFALO, NEW YORK, BY NELLIE S. COLEMAN, EXECUTRIX, OF REVERE, MASSACHUSETTS.

ANTIFOULING COMPOSITION.

1,421,914.

Specification of Letters Patent.

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No Drawing.

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To all whom it may concern:

Be it known that GEORGE D. COLEMAN, deceased, late a citizen of the United States, residing at Buffalo, New York, did invent certain new and useful Improvements in Antifouling Composition; and I, NELLIE S. COLEMAN, of Revere, in the county of Suffolk and State of Massachusetts, his executrix, do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention relates to a compound suitable for application to the bottom of a vessel or to any other object which is exposed to the destructive effects of sea-water and the organisms therein.

Various compounds have been heretofore proposed for use in coating the bottoms of vessels or other sub-aqueous surfaces, these compounds containing copper in finely-divided form with the object of preventing the penetration of, or adhesion to the surface so protected, of barnacles, teredos and other aquatic organisms, upon which the salts which are formed by the action of the water upon the copper have a poisonous or repellant effect. The present invention relates to a compound of this character, and the object of the invention is to produce a compound which will form a coating which not only is strong, durable and tenacious, but which also is so composed that it will continuously present, at its exposed surface, sufficient copper or the salts thereof to effectually repel or destroy organisms damaging to the surface protected.

In previously proposed compounds of the kind in question copper, usually in finely-divided metallic form, has been combined with a binder or matrix of some water-repellant carbonaceous substance, such as asphalt, oil-paint, or varnish, the copper particles being disseminated throughout the binder. Such coatings have, however, been lacking in mechanical strength and durability, and they have also had the disadvantage that only the copper particles close to the outer surface have been available for any effective action, the particles buried within the body of the binder being too effectually preserved from contact with the water, and thereby

protected from its solvent action. To avoid the disadvantages of such previously-proposed compounds the present inventor has previously devised methods of producing protective coatings in which the copper particles are all located at the outer surface, so as to be entirely available for solution and effective action. These methods involve the application of the copper particles to a coat of moist or tacky paint or binding material and the subsequent operation of hammering, burnishing, or soldering the particles to bring them to a smooth and substantially continuous surface.

The inventor has discovered that an effective antifouling coating may be produced without the operations last referred to, and by the use of a compound throughout which the copper particles are uniformly disseminated, instead of being segregated at the surface, provided the binder with which the copper is incorporated is of such a character as to permit water to penetrate to some extent within its outer surface and thus have access to the copper particles incorporated therein, and he has discovered that a binder consisting principally or wholly of hydraulic cement has the required characteristics, and produces, in addition, a coating having substantially greater strength and durability than those in which the binding material is of a carbonaceous or organic character, such as the tarry, resinous, or oily substances previously proposed for this purpose. Accordingly, the present invention, in its broadest aspect, resides in the use, as the basis of the compound, of a hydraulic cement such as Portland cement, intimately mixed with copper or cupric material in a finely-divided form.

While the hydraulic cement may be used without admixture of other substances than the copper or cupric material, it is preferable to add to the cement comparatively small proportions of several other substances by which its physical and chemical characteristics are somewhat modified. To increase the hardness, and the resistance to abrasion, of the coating produced by the present compound, it is desirable to use a certain amount of sand, either natural sharp sand or the equivalent produced by crushing quartz. To increase the tensile strength of the material

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mineral fiber, such as mineral-wool or the fibrous forms of asbestos and magnesia, may be added to the compound. To increase the tenacity and facilitate hardening of the compound, calcium-hydroxide may be employed.

The principal content of copper may be in the form either of metallic copper in fine particles, or of some ore or concentrate rich in copper. This principal content of copper is thus in a form in which it is substantially insoluble in pure water, and in which solution of the copper takes place only gradually in sea-water, in consequence of reactions produced by the sodium-chlorid dissolved in the water. In addition, however, to this principal content of the copper, it is desirable to use a comparatively small amount of copper in the form of a soluble salt, such as acetate or sulphate of copper. This soluble salt performs two useful functions. In the first place, it has an acid reaction by which it neutralizes the caustic alkali of the cement, and thereby prevents this alkali from injuriously affecting the anchoring coat of paint or varnish upon which the present compound may be spread. In the second place, the soluble copper-salt is immediately available and soluble at the surface of the coating formed from the present compound, so that even when the coating is first put into use and before the sodium-chlorid of the water has reacted to any substantial extent upon the relatively insoluble copper or cupric material, there is present at the surface of the coating a sufficient quantity of copper in immediately soluble form to secure the performance of the anti-fouling function of the coating.

Since the hydraulic cement is of a somewhat porous and hygroscopic character, the action of the sea-water is not limited to the surface of the cement, but the water may penetrate more or less into the body of the cement, thereby coming into contact with the copper embedded therein. The solution and removal of the copper at or near the surface of the cement, by increasing the porosity of the coating at this point, tends to promote flaking or erosion of the surface so far as is necessary to afford access of the water to the copper particles more deeply embedded in the coating, and in consequence of these facts a large part, if not the whole, of the copper ultimately becomes available for the production of salts by which fouling of the surface is prevented.

The characteristic just described radically distinguishes the present compound, and the coating produced by it, from compounds in which water-repellant substances are employed in place of the hygroscopic and comparatively porous cement of the present invention. Indeed, it is preferable to modify and diminish, to some extent, the natural porousness and hygroscopic character im-

parted to the compound by the cement, and for this purpose a small quantity of water-repellant material may be incorporated in the mixture. It has been found that paraffine-wax is a suitable material for this purpose.

The ingredients, and the proportions thereof, of a compound which has been found suitable for carrying out the present invention are as follows:

	Parts by weight.
Hydraulic cement	100
Finely-divided metallic copper or rich copper-ore or concentrates of copper	108 80
Sand or ground quartz	50
Mineral fiber	8
Calcium hydroxid	8
Paraffine-wax	5
Acetate or sulphate of copper	6 85

The sand or quartz may be of a fineness such as to pass through a screen of 50 or 60 mesh, and the paraffine-wax may have a melting point of approximately 135 degrees Fahrenheit.

The foregoing ingredients may be mingled in the following manner. The calcium-hydroxid, the acetate or sulphate of copper, and the paraffine-wax are triturated, together with a weight of dry cement equal to the combined weight of the other ingredients, in a suitable mill, and the remainder of the cement is gradually added to the mixture. The compound so produced is then transferred to a suitable mixing machine and the sand, the cupric material, and the mineral fiber are added to and mixed with the other ingredients, but without grinding.

Dry coloring-matter, such as a dark chrome green, may be added to the mixture if desired, and the compound may be packed dry and so kept until it is to be used for the production of an anti-fouling coating.

In producing a coating with the compound of the present invention, this compound may be mixed either with pure water, or with an emulsion comprising water and 20 per cent, more or less, of crude petroleum of low specific gravity, and the plastic mixture so formed may be spread upon the surface which is to receive it, either in the form of a spray or by the use of a trowel or other suitable tool. In order to permit adhesion of the anti-fouling compound to the surface to which it is applied, and also to prevent electrolytic or chemical action between the compound and the surface, in the case of a metallic surface, such as that of the steel bottom of a ship, it is preferable to coat this surface first with one or more coats of oil-paint or varnish, or other water-repellant material, and to apply to, and partially embed in, the anchoring layer so formed, while it is still moist and tacky, particles of bonding and insulating ma-

terial such as sand or brick-meal to afford a rough surface to which the cementitious compound will adhere, and to prevent or limit direct contact between the cementitious compound and the anchoring layer.

alt 10 The compound of the present invention, instead of being mixed with water or an emulsion of water and non-drying oil as above described, may be mixed with a drying oil such as linseed oil, and thus rendered plastic and suitable for application as a coating. The use of water is preferable, however, as the useful functions of some of the ingredients are more or less impaired by the presence of a water-repellant binder such as dried oil.

20 The invention is not limited to the embodiment thereof hereinbefore described, but may be embodied in various other forms within the scope of the following claims.

The invention claimed is:—

1. An anti-fouling composition comprising an intimate mixture of hydraulic cement, cupric material substantially insoluble in water, and a soluble salt of copper. 25

2. An anti-fouling composition comprising an intimate mixture of hydraulic cement, and finely divided material containing copper in a substantially water insoluble form and a water soluble salt of copper. 30

3. An anti-fouling composition comprising an intimate mixture of hydraulic cement, calcium hydrate, and cupric material including a soluble acid salt.

4. An anti-fouling composition comprising an intimate mixture of hydraulic cement, calcium hydrate, sand, mineral fiber, paraffine-wax, and cupric material. 35

NELLIE S. COLEMAN,

Executrix of George D. Coleman, Deceased.