

DESCRIPTION

COPPER PYRITHIONE AGGREGATES AND USE OF SAME

Field of the Invention

[0001] The present invention relates to copper pyrithione aggregates and use of the same. For details, it relates to copper pyrithione aggregates produced by reaction of water-soluble metal pyrithione or ammonium pyrithione, and double salt of inorganic copper (II) salt and inorganic ammonium salt, or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt in an aqueous medium of pH more than 4- less than 9, and their production method. In addition, it relates to an antifoulant for use in water wherein the particle size of copper pyrithione aggregates produced by reaction of water-soluble metal pyrithione or ammonium pyrithione, and double salt of inorganic copper (II) salt and inorganic ammonium salt, or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt in an aqueous medium of pH 1- less than 9, falls within the range of 5.5- less than 9 μm by median value on the premise that the particles have a one peak pattern of distribution of particle size.

Background of the Invention

[0002] For production of copper pyrithione, a method of addition of surfactant is disclosed in patent document 1 in order to prevent gelation occurring in production process and to promote the reaction. When inorganic copper (II) salt is added to an aqueous solution of pyrithione alkali metal salt under the condition of pH 3-8 as described in the claims of the patent, fine crystals of basic copper salt are precipitated previously before the forming of copper pyrithione. Although copper pyrithione can be obtained by reaction of slightly-soluble precipitate of basic copper salt and pyrithione alkali metal salt, it turns into very sticky liquid. This is the actual situation of the phenomenon called gelation. Although the reaction can proceed by adding a surfactant, the particles of copper pyrithione produced are as small as only several micrometers. They are not easy to be filtrated, which is taken as its disadvantage. In addition, the basic copper salt which remains as an impurity in copper pyrithione products may

possibly cause gelation during the storage of paint when formulated in ship-bottom paint.

[0003] In patent document 2, a production method of copper pyrithione is disclosed wherein, aqueous solutions of pyrithione metal salt and inorganic copper (II) salt are reacted at high temperature within pH range of 1.6 - 3.2, and then inorganic copper (II) salt is added thereto, followed by conducting heating treatment. In the first step of this method, due to the production condition of long time reaction under low pH and high temperature, bispyrithione (dimer) can be produced easily by oxidation of pyrithione acid. Thus in the second step, a method of thermal decomposition of bispyrithione and addition of inorganic copper (II) salt at the same time is employed to increase the purity of copper pyrithione. Although the copper pyrithione of high purity can be obtained, there is a disadvantage of high production cost due to increased production process. Additionally, in the second step, although the yield is limited, the formation of the basic copper salt described above is unavoidable. Because small amount of basic copper salt is produced, the average particle size of the copper pyrithione obtained by the production method of this patent is significantly larger than that of copper pyrithione obtained by the production method of the above-mentioned patent document 1. Nevertheless, it doesn't exceed 5 μm when using centrifugation type of particle size distribution analyzer 'CAPA-500' (Horiba Ltd.), as shown in the example.

[0004] In patent document 3, taking a certain range of particle size as component, an antifouling composition is disclosed in which pyrithione metal salt with its defined ratio range of particle size was used as active ingredient. In terms of copper pyrithione among pyrithione metal salt, four examples of D (0.5) of median values were shown in working and comparison examples, a sample of pulverized product, a sample of wet filtrate, a sample of a mixture of pulverized and un-pulverized products and a sample of un-pulverized product (in comparison example). The measured results of pulverized product and wet filtrate were 2-3 μm . Meanwhile, that for the mixture of pulverized and un-pulverized products was over 5 μm . However, the product of copper pyrithione was obtained by pulverizing its dried block as described in Example 1 of patent document 2. In the production process, dried block is certainly formed in drying process from wet cake after rinsing and filtration. Certainly, un-pulverized product cannot be taken as product.

The method for obtaining undried product with average particle size of product level is limited to special treatment of samples in small amount in laboratory, which is not aimed at production. In addition, the method of measuring the particle distribution of wet cake as an aqueous dispersion is also possible. Although this method is possible in laboratory, it can be said that the results obtained by using this method cannot be applied to copper pyrithione products considering that antifoulant paints for ship-bottom and antifoulant for fish-farming net are oil-based products and extremely hydrophobic. Therefore, the measured result of 5.8 μm of the mixture of pulverized and un-pulverized products and the measured result of 8.3 μm of the un-pulverized product are not suitable as measured results of the average particle size of copper pyrithione products. Only the result of pulverized product should be referred from the viewpoint of possible industrial applicability.

Prior Art Literatures

Patent Documents

- [0005] Patent document 1 : JP3062825
 Patent document 2 : JP3532500
 Patent document 3 : JP4653642
 Patent document 4 : JP5594619

Disclosure of the Invention

Problems to be Resolved by the Invention

[0006] There were two future tasks about improving copper pyrithione which has been known world-wide as a major antifoulant for ship-bottom paint. One was to control its elution from coating film to develop a product having long lasting antifouling effect from the viewpoint of marine environmental protection. The other was to develop a product with particles that brings minimized dusting in order to improve its safety at work site.

Means of Solving the Problems

[0007] The present inventor succeeded in producing copper pyrithione aggregates composed of smaller cylindrical and tabular particles, which are different from acicular crystals of conventional copper pyrithione by using

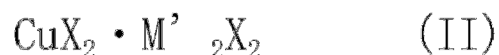
double salt of inorganic copper (II) salt and inorganic ammonium salt instead of inorganic copper (II) salt, which is a raw material for producing conventional copper pyrrhione. As the results, it was found that the elution to sea water of particles of copper pyrrhione aggregates with average particle size of 5.5-less than 9 μm and mainly in spherical and ellipsoid spherical shape can be controlled and the risk of inhalation at work site can be reduced. The above problems were resolved.

That is, the present invention provides;

- (1) Copper pyrrhione aggregates produced by reaction of water-soluble metal pyrrhione or ammonium pyrrhione represented by general formula (I):



wherein, M represents a monovalent or bivalent metal, or ammonium, Py represents 2-pyridylthio-N-oxide group, and $n = 1$ or 2 , and double salt of inorganic copper (II) salt and inorganic ammonium salt or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt represented by general formula (II):



wherein, X represents an anion selected from Cl, $1/2\text{SO}_4$ or NO_3 , and M' represents ammonium or alkali metal, in an aqueous medium of pH more than 4-less than 9,

- (2) Production method of copper pyrrhione aggregates, characterized by being produced by reaction of water-soluble metal pyrrhione or ammonium pyrrhione represented by general formula (I):



wherein, M represents a monovalent or bivalent metal, or ammonium, Py represents 2-pyridylthio-N-oxide group, and $n = 1$ or 2 , and double salt of inorganic copper (II) salt and inorganic ammonium salt or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt represented by general formula (II):



wherein, X represents is an anion selected from Cl, $1/2\text{SO}_4$ or NO_3 , and M' represents ammonium or alkali metal, in an aqueous medium of pH

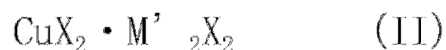
more than 4-less than 9,

- (3) Copper pyrithione aggregates produced by reaction of water-soluble metal pyrithione or ammonium pyrithione represented by general formula (I):



wherein, M represents a monovalent or bivalent metal, or ammonium, Py represents 2-pyridylthio-N-oxide group, and $n = 1$ or 2 ,

and double salt of inorganic copper (II) salt and inorganic ammonium salt or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt represented by general formula (II):



wherein, X represents is an anion selected from Cl, $1/2SO_4$ or NO_3 , and M' represents ammonium or alkali metal, in an aqueous medium of pH 1-less than 9, wherein, the particle size falls within the range of 5.5-less than 9 μm by median value on the premise that the particles have a one peak pattern of distribution of particle size,

- (4) The copper pyrithione aggregates described in the above-mentioned (1) or (3), wherein, M is a metal selected from a group consisting of sodium, potassium, calcium and magnesium,
- (5) The production method of the copper pyrithione aggregates described in the above-mentioned (2), wherein, M is a metal selected from a group consisting of sodium, potassium, calcium and magnesium,
- (6) The copper pyrithione aggregates described in the above-mentioned (1), (3) or (4), wherein, the inorganic copper (II) salt is copper (II) chloride or copper (II) sulfate,
and the inorganic ammonium salt is ammonium chloride or ammonium sulfate, and the inorganic alkali metal salt is sodium chloride or sodium sulfate,
- (7) The production method of copper pyrithione aggregates described in the above-mentioned (2) or (5), wherein, the inorganic copper (II) salt is copper (II) chloride or copper (II) sulfate, and the inorganic ammonium salt is ammonium chloride or ammonium sulfate, and the inorganic alkali metal salt is sodium chloride or sodium sulfate,
- (8) The copper pyrithione aggregates according to the above-mentioned (3), wherein, median value of particles of copper pyrithione aggregates falls

within the range of 5.5-less than 9 μm on the premise of using fine powder grinding machine,

- (9) An antifoulant for use in water which contains copper pyrithione aggregates according to the above-mentioned (1),
- (10) An antifoulant for use in water which contains copper pyrithione aggregates according to the above-mentioned (3) or (8) and
- (11) An antifoulant for use in water for ship-bottom paints or fish-farming net according to the above-mentioned (9) or (10).

[0008] For uses in the production of the copper pyrithione aggregates of present invention, sodium pyrithione is exemplified as preferable metal pyrithione; copper (II) sulfate or copper (II) chloride are exemplified as preferable inorganic copper (II) salt; ammonium sulfate or ammonium chloride are exemplified as preferable inorganic ammonium salt; and sodium sulfate or sodium chloride are exemplified as preferable inorganic alkali metal salt.

[0009] For use in present invention, double salt of copper chloride and ammonium chloride ($\text{CuCl}_2 \cdot 2(\text{NH}_4)\text{Cl} \cdot 2\text{H}_2\text{O}$) or double salt of copper sulfate and ammonium sulfate ($\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) are exemplified as preferable double salt of inorganic copper (II) salt and inorganic ammonium salt. Double salt of copper sulfate and sodium sulfate ($\text{CuSO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$) or double salt of copper sulfate and potassium sulfate ($\text{CuSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) are exemplified as the preferable double salt of inorganic copper (II) salt and inorganic alkali metal salt. These double salts can generally be obtained as crystals by concentrating an aqueous sulfuric acid solution or hydrochloric acid solution of calculated amount of inorganic copper (II) salt and inorganic alkali metal salt or inorganic ammonium salt. However, it is efficient and preferable to use the above-mentioned concentrated solution directly as aqueous solution of raw material for producing copper pyrithione aggregates of present invention for the reaction with aqueous solution of metal pyrithione without taking the crystals out of the concentrated solution.

When inorganic ammonium salt is partly replaced by inorganic alkali metal salt, the ratio of inorganic alkali metal salt is 10-90%, preferably 30-70%. There is no effect of replacement when the ratio is lower than 10% and aggregates from ammonium cannot be obtained when the ratio was higher than 90%. The advantage of using inorganic alkali metal salt to

replace partly inorganic ammonium salt can be achieved when reaction is conducted in conditions of high pH and comparably high temperature. In these conditions, the quantity of ammonia generated from inorganic ammonium can be controlled and effect of smooth stirring can be expected. However, since the impurity of inorganic alkali metal salt in copper pyrithione aggregates obtained cannot be removed easily, the content of the impurity tends to increase and particles elongate, which brings negative effects unavoidably to quality and particle size control of copper pyrithione aggregates obtained. Therefore, it is recommended to use only inorganic ammonium salt without using inorganic alkali metal salt when reacting in conditions of low pH and low temperature, that is, the condition wherein, almost no ammonium is generated. Either of the methods to be chosen depends on the conditions, scale and facilities of manufacture.

[0010] In the conventional method for producing copper pyrithione by reaction of aqueous solutions of metal pyrithione and inorganic copper (II) salt, at pH range of 4-8, basic copper salt (for example, basic copper sulfate, $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$) is generated before copper pyrithione is produced. Thus the reaction turns out to be carried out between solid and liquid phase. Not only the efficiency of reaction decreases but also the viscosity increases. The reaction cannot continue without using surfactant as described in patent document 1. Meanwhile, in the reaction of the present invention, which is a reaction between aqueous solutions of metal pyrithione and double salt of inorganic copper (II) salt and inorganic ammonium salt, or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt, inorganic ammonium salt or inorganic alkali metal salt which have greater binding force than copper hydroxide combine with inorganic copper (II) salt. Therefore, the reaction between liquid phases continues without production of basic copper salt. There is an advantage that the reaction in condition of pH 4-8 can be carried out smoothly without necessity of using surfactant. The preferable pH range is 1-less than 9 for producing copper pyrithione aggregates of the present invention. The pH range of 1-4 has been applied previously by the same inventor (patent document 4). When reacting in pH condition of higher than 9, inorganic ammonium salt, which is a necessary raw material, not only prevent the formation of aggregates to replace inorganic alkali salt, but also emits ammonia to cause problematic odor.

[0011] In the conventional method for producing copper pyrrhione by reaction of aqueous solutions of metal pyrrhione and inorganic copper (II) salt, the reaction is conducted at high temperature of over 70°. Meanwhile, in the method of present invention, that is, the reaction between aqueous solutions of metal pyrrhione and double salt of inorganic copper (II) salt and inorganic ammonium salt, or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt, the reaction temperature is 10-40°, preferably 15-30° of room temperature. If the reaction is conducted at high temperature, the particles turn larger and preferable aggregates cannot be obtained. In addition, problematic odor is emitted.

[0012] The copper pyrrhione aggregates produced from sodium pyrrhione and double salt of copper (II) sulfate and ammonium sulfate as raw materials according to the production method of present invention were pulverized to particles with average particle size of about 10 µm and dispersed in water. When heated at 80° for 30 minutes, ammonia odor was emitted slightly and several 10% of the aggregates were decomposed. The substance which contributes to the formation of copper pyrrhione aggregates is considered to be ammonium ion which has affinity for copper. But from the analytical results of X-ray diffraction, ammonium sulfate was not confirmed and the substance was not identified. Since no difference was found by comparing with the charts of X-ray diffraction analysis of copper pyrrhione, it was considered that ammonium was adhered to copper pyrrhione in a non-crystal form. After rinsing thoroughly so that the Na content was below 1 ppm, the purity of copper pyrrhione aggregates was 98.2-98.6% when measured by HPLC method. From this result, the ammonium content in the copper pyrrhione aggregates was estimated to be about 1.4%. Meanwhile, as for the possibility of contribution of sodium sulfate to the formation of copper pyrrhione aggregates, since it is clear that when copper pyrrhione aggregates were rinsed thoroughly, the Na content was about 0.1 ppm as shown in Example 2 and it is not retained in the aggregates, it can be considered that there is no such possibility.

[0013] According to the production method of copper pyrrhione aggregates of present invention, the reaction product was rinsed and filtered. The solid obtained after drying, is roughly large particles of aggregates with several 100 µm in diameter. When pulverizing them by shearing stress such as rubbing force in mortar, part of the particles turn into micro particles

and the distribution of particle size shows a pattern of two peaks, one of comparatively large particles and the other of micro particles (patent document 4). However, when pulverizing by pushing force on their surface such as using a ball mill as fine powder grinding machine, normal distribution of particle size or its similar pattern of one-peak distribution can be obtained. This distribution pattern of particle size can be confirmed by using particle size distribution analyzer of laser diffraction type, such as LA-920 (Horiba Ltd.). The copper pyrithione aggregates obtained by the pulverizing method of present invention do not actually contain micro particles. Therefore, they are excellent in terms of elution control from coating film of antifoulant for ship-bottom paint and fish-farming net compared with the particles of the above aggregate which have both micro and comparatively large particles. The preferable particle size range of antifoulant for ship-bottom paint and fish-farming net is 1-30 μm and their median values are 5.5-less than 9 μm by assuming that the lower limit of 5.5 μm is measured by particle size distribution analyzer of centrifugation type, CAPA-500 (Horiba Ltd.). This is due to the fact that the average particle size of 1-5 μm which is claimed in patent document 2 was measured by CAPA-500.

[0014] So far there were safety concerns about dusting inhalation at work site when handling copper pyrithione as powder. Particularly the fact that conventional copper pyrithione is in form of comparably hard and acicular crystals, is problematic. Methods for such as enlarging their particles by using surfactant and covering them with substance like oily resin to make paste have been suggested. These methods are effective, but they are unavoidably cost consuming because of secondary treatment of copper pyrithione powder. The copper pyrithione aggregates of present invention have larger particles and they are flowable. They are easy to handle and cause less dusting. And there is no problem caused by acicular crystals. Therefore, secondary treatment is not needed and the risk of health damage is greatly reduced compared with conventional product even when handling the powder.

[0015] The elution speed of copper pyrithione from coating film of antifoulant for ship-bottom paint or fish-farming net is affected by factors such as the property of coating film, the navigation speed of ship, the speed of ocean current and adhesion of fouling organisms, as well as the surface

area of copper pyrithione and temperature of sea water. Although its difference cannot be accessed simply by the ratio of surface area of copper pyrithione, the surface area of the copper pyrithione aggregates of present invention with average particle size (median value) of 5.5-less than 9 μm , is 1.5-4 folds larger than that of commercially available copper pyrithione and due to the effect of elution delay on the copper pyrithione aggregates by the coexistence of aggregates forming substances, the speed of its elution to sea water is significantly delayed compared with conventional copper pyrithione. As the result, not only the persistency of antifouling effect at high water temperature such as in tropical waters is improved, but also the emission of copper pyrithione to sea water can be reduced, which is desirable from the viewpoint of marine environmental protection.

The copper pyrithione aggregates of present invention are formulated in antifouling paint for ship-bottom, in which silyl acrylate resin, zinc acrylate resin and copper acrylate resin and their copolymer resins are used as binders and in antifoulant for fish-farming net in which flexible resins such as acrylate resin are used as binders. In each case, they are usually used together with cuprous oxide.

Effect of the Invention

[0016] While the conventional copper pyrithione is in form of acicular crystals with median values of less than 5 μm , the copper pyrithione aggregates of present invention are individually shorter and smaller particles, but as aggregates with median values of 5.5-less than 9 μm and they have excellent liquidity. Thus the risk of inhalation at work site is reduced significantly. In addition, the elution into sea water is greatly decreased when used as antifoulant for ship-bottom paint and fish-farming net and the persistency of antifouling effect is improved.

Brief Description of the Drawings

[0017] [Fig. 1] is a chart showing X-ray diffraction pattern of the copper pyrithione aggregates obtained in Example 1.

[Fig. 2] is a chart showing X-ray diffraction pattern of commercially available copper pyrithione.

[Fig. 3] is a chart showing exothermic peak temperature in DTA/TGA of the copper pyrithione aggregates obtained in Example 1.

[Fig. 4] is a chart showing median values (50%) from particle distribution of the copper pyrithione aggregates obtained in Example 1 (Centrifugation type, 'CAPA-500' Horiba Ltd.).

[Fig. 5] is a chart showing median values (50%) from particle distribution of the copper pyrithione aggregates obtained in Example 1 (Laser diffraction type, 'LA-920' Horiba Ltd.).

[Fig. 6] is a scanning electron microscopy picture of the copper pyrithione aggregates obtained in Example 1.

[Fig. 7] is a chart showing median values (50%) from particle distribution of the copper pyrithione aggregates obtained in Example 2 (Laser diffraction type, 'LA-920' Horiba Ltd.).

[Fig. 8] is a chart showing median values (50%) from particle distribution of the copper pyrithione aggregates obtained in Example 3 (Laser diffraction type, 'LA-920' Horiba Ltd.).

[Fig. 9] is a scanning electron microscopy picture of the copper pyrithione aggregates obtained in Example 3.

[Fig. 10] is a chart showing X-ray diffraction pattern of the copper pyrithione aggregates obtained in Example 4.

[Fig. 11] is a chart showing median values (50%) from particle distribution of the copper pyrithione aggregates obtained in Example 4 (Centrifugation type, 'CAPA-500' Horiba Ltd.).

[Fig. 12] is a scanning electron microscopy picture of the copper pyrithione aggregates obtained in Example 4.

Mode for Carrying Out the Invention

[0018] The present invention will be illustrated in details in reference to the following examples.

Example 1

[0019] To a reaction vessel (5 L) were added 125 g (0.5 mole) of copper sulfate pentahydrate and 66 g (0.5 mole) of ammonium sulfate and 1.8 L of their aqueous solution was prepared. After 20 mL of 10% sulfuric acid was added, the solution was adjusted to pH 2. Then, 300 mL of 40% aqueous solution of sodium pyrithione (density: 1.22) was diluted with water to make 1.2 L of aqueous solution. To 1.8 L of aqueous solution of copper sulfate and ammonium sulfate was added dropwise 1.2 L of aqueous solution of

sodium pyrrhithione over 2 hours at 20°C under stirring. 3 L of slurry of copper pyrrhithione aggregates obtained was then filtered under reduced pressure. The solid remained after the filtration was put back to the vessel and was added with water to make 3 L of slurry of copper pyrrhithione aggregates again. After stirring, it was filtered again under reduced pressure. The operation was repeated twice. The solid obtained was put in a dryer and dried over night at 80°C. After being crushed into small pieces, the solid was pulverized over 40 minutes by using a ball mill. The yield was about 150 g.

Small amount of the sample was taken from it and X-ray diffraction analysis was conducted. As a result, exactly the same X-ray diffraction pattern with that of commercially available copper pyrrhithione (KOLON Life Science Ltd.) was shown (Fig. 1 and 2). In addition, the heat generation peak temperature of DTA/TGA was 280°C. Neither heat absorption nor heat generation peaks indicating the impurities were confirmed (Fig. 3). The exothermic peak temperature of recrystallized product of copper pyrrhithione was 276°C. Meanwhile, the temperature of commercially available copper pyrrhithione was 282-285°C. Therefore, the copper pyrrhithione aggregates obtained in this example was highly pure in spite of the fact that they contain trace amount of combined ammonium. Its real purity when measured by using HPLC method was 98.2%. In addition, the average particle size was 5.9 µm (Fig. 4) when measured by using 'CAPA-500' of centrifugation type (Horiba Ltd.) or 6.48 µm (Fig. 5) when measured by using 'LA-920' of laser diffraction type (Horiba Ltd.) (Median value respectively, dispersion medium: 0.2% aqueous solution of DEMOL-N). Besides, it was confirmed by SEM pictures that the copper pyrrhithione aggregates obtained in this example were aggregates of particles in cylindrical and tabular shape with small aspect ratio (Fig. 6).

Example 2

[0020] Copper pyrrhithione aggregates were synthesized by using the same method as in Example 1 and its slurry was taken in a beaker (500 mL). It was rinsed and filtered by using a 5A filter paper of 18 cm diameter. The residue was put back to the beaker and added with water. After stirring, it was rinsed and filtered by using a 5A filter paper. The operation was repeated three times. The solid from which water was squeezed out was

put into a drier and dried at 60°C for 6 hours. The small pieces obtained were pulverized over 40 minutes by using a ball mill. Small amount of the sample was taken from it and X-ray diffraction analysis was conducted. As a result, exactly the same X-ray diffraction pattern as that of copper pyrithione was shown. In addition, the average particle size was 5.79 µm (Fig. 7) when measured by using 'LA-920' of laser diffraction type (Horiba Ltd.) (Median value, dispersion medium: 0.2% aqueous solution of DEMOL-N). Furthermore, the sodium content in the sample was 0.09 µg/mg when measured by atomic absorption analysis. Almost no sodium sulfate remained as side product.

Example 3

[0021] 12.5 g of copper sulfate pentahydrate and 6.6 g of ammonium sulfate were mixed in a beaker (1 L) and 360 mL of their aqueous solution was prepared. The pH was adjusted to 4.1 with 1% aqueous solution of sodium hydroxide. Then, 30 mL of 40% aqueous solution of sodium pyrithione (density: 1.22) was diluted with water to make 240 mL of aqueous solution. The production of basic copper sulfate was not confirmed. To 360 mL of aqueous solution of copper sulfate and ammonium sulfate, 240 mL of aqueous solution of sodium pyrithione was added dropwise under stirring over 30 minutes at 26°C. The pH value at the end point of the reaction was 7.3. After the reaction, 600 mL of the slurry of copper pyrithione aggregates was allowed to stand overnight. And then it was rinsed and filtered with a 5A filter paper. Liquid solid remaining on the filter paper was put back to the beaker and added with water. After stirring, it was filtered again. The operation was repeated twice. The solid from which water was squeezed out was put into a drier and dried at 60°C for 6 hours. The small pieces obtained were pulverized over 30 minutes by using a ball mill. The yield was about 150 g. The purity was 98.6% when measured by HPLC method.

Small amount of the sample was taken from it and X-ray diffraction analysis was conducted. As a result, exactly the same X-ray diffraction pattern as that of copper pyrithione was shown. In addition, when pulverized for 30 minutes, the average particle size was 7.43 µm (Fig. 8) when measured by using 'LA-920' of laser diffraction type (Horiba Ltd.) (Median value, dispersion medium: 0.2% aqueous solution of DEMOL-N). Furthermore, it was confirmed by SEM pictures that the copper pyrithione

aggregates obtained in this example were aggregates of particles in cylindrical and tabular shape with small aspect ratio (Fig. 9).

Example 4

[0022] Instead of the 6.6 g of ammonium sulfate in Example 3, 3.3 g of ammonium sulfate and 3.6 g of sodium sulfate were used. The pH was adjusted to 6.4 with 1% aqueous solution of sodium hydroxide. The reaction was conducted at 30°C by using the same method as that in Example 3. The pH value at the end point of reaction was 7.8. No ammonia odor was detected. After the reaction, the slurry of copper pyrithione aggregates was rinsed and filtered in the same way as in Example 3. The small pieces obtained after drying were pulverized for 15 minutes by using a ball mill. Small amount of the sample was taken from it and X-ray diffraction analysis was conducted. As a result, exactly the same X-ray diffraction pattern as that of copper pyrithione was shown (Fig. 10). In addition, the average particle size was 8.5 µm (Fig. 11) when measured by using 'CAPA-500' of centrifugation type (Horiba Ltd.) (Median value, dispersion medium: 0.2% aqueous solution of DEMOL-N). Furthermore, it was confirmed by SEM pictures that the copper pyrithione obtained in this example is aggregates of cylindrical particles with small aspect ratio (Fig. 12).

Example 5

[0023] In order to investigate the elution of antifoulant for fish-farming net from coating film, the following ingredients apart from other components which potentially affect the elution were mixed homogeneously to obtain an antifoulant for fish-farming net.

Copolymer of butyl acrylate and methyl methacrylate (solution of 50 w/w% xylene)	20.0 w/w%
Copper pyrithione aggregates of Example 1 (compositions I) or commercially available copper pyrithione (compositions II)	4.0 w/w%
Xylene	76.0 w/w%
Total	100.0 w/w%

Note: commercially available copper pyrithione; copper pyrithione manufactured by A Co. (acicular crystals), average particle size: 4.8 µm (CAPA-500)

Knotless nets made from polyethylene (6 knots, 400 denier, 6 pieces)

were soaked in the antifoulant for fish-farming net whose compositions (I and II) are described above and dried. The speeds of elution into water of copper pyrithione aggregates and copper pyrithione in the antifoulant for fish-farming net was investigated by over time determination of the concentration of copper dissolved.

Preparation of samples

Knotless nets made from polyethylene were soaked in antifoulant for fish-farming net with compositions I and II in Example 6 and dried. The nets were cut small so that each piece contained 1 g of the antifoulant. Each sample was soaked in 250 mL of purified water and then stirred at room temperature for 1, 4 and 7 days (6 samples in total). The samples were filtered using 5C filter paper and then membrane filter with average pore size of 0.45 μm . To the filtrates was added nitric acid to make 0.1 mol/L solutions for the determination.

For comparison, the solubility in water of copper pyrithione aggregates of description I and that of copper pyrithione of description II was determined using the same method under stirring for 24 hours.

Method of determination

ICP emission spectroscopic analysis ('ICPS-2000', Shimadzu Corporation)

The results of the determination are shown in Table 1.

[0024] Table 1 Concentrations of copper components eluted (mg/L)

Samples: I. Copper pyrithione aggregates in Example 1

Average particle size; 5.9 μm (CAPA-500)

II. Copper pyrithione manufactured by A Co.

Average particle size; 4.8 μm (CAPA-500)

Sample	Stirring time	Copper eluted from antifoulant for fish-farming net	Copper dissolved from copper pyrithione
I	1 day	0.01	0.03
	4 days	0.02	
	7 days	0.02	
II	1 day	0.04	0.07
	4 days	0.06	
	7 days	0.07	

The above results show that the copper pyrithione aggregates of present invention eluted more slowly from coating film of antifoulant for fish-farming

net than commercially available copper pyrithione in comparison with the difference in their average particle size. This may possibly due to the shape of the aggregates. As for the elution to water from coating film of ship-bottom antifoulant paint, this method of determination cannot be applied because the paint is usually formulated with cuprous oxide. However, considering the fact that acrylate resin used in antifouling ship-bottom paint is similar with the antifoulant for fish-farming net, the results of the present example is considerably the same or show similar tendency with the case of antifouling ship-bottom paint.

Example 6

[0025] The following components were mixed homogeneously to obtain ship-bottom paint.

Copolymer of methyl methacrylate and triisopropylsilyl acrylate (2:3, solution of 50 w/w% xylene)	36 w/w%
Cuprous oxide	32 w/w%
Zinc oxide	4 w/w%
copper pyrithione aggregates of Example 3	3 w/w%
Titanium white	2 w/w%
Red iron oxide	2 w/w%
Fatty acid amide wax (20%)	2 w/w%
Xylene	19 w/w%
Total	100 w/w%

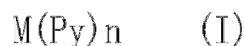
Abnormal phenomenon such as gelation was not confirmed neither immediately after the preparation of the paint nor 3 months later.

Industrial Applicability

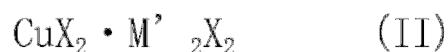
[0026] Since the copper pyrithione aggregates of present invention are easier to handle because they cause less dusting compared with conventional commercially available copper pyrithione. Besides, they have larger particles with average size of 5.5-less than 9 μm by median value. As the result of elution delay from coating film of antifouling ship-bottom paint and antifoulant for fish-farming net, they can be possibly used as antifoulant with both long-lasting antifouling effect especially in the tropical marine waters and small amount of emission to environment.

CLAIMS

1. Copper pyrithione aggregates produced by reaction of water-soluble metal pyrithione or ammonium pyrithione represented by general formula (I):

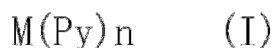


wherein, M represents a monovalent or bivalent metal, or ammonium, Py represents 2-pyridylthio-N-oxide group, and n=1 or 2,
and double salt of inorganic copper (II) salt and inorganic ammonium salt or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt represented by general formula (II):

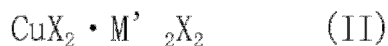


wherein, X represents an anion selected from Cl, $\frac{1}{2}SO_4$ or NO_3 and M' represents ammonium or alkali metal, in an aqueous medium of pH more than 4-less than 9.

2. Production method of copper pyrithione aggregates, characterized by being produced by reaction of water-soluble metal pyrithione or ammonium pyrithione represented by general formula (I):



wherein, M represents a monovalent or bivalent metal, or ammonium, Py represents 2-pyridylthio-N-oxide group, and n=1 or 2,
and double salt of inorganic copper (II) salt and inorganic ammonium salt or double salt in which inorganic ammonium salt is partly replaced by inorganic alkali metal salt represented by general formula (II):



wherein, X represents an anion selected from Cl, $\frac{1}{2}SO_4$ or NO_3 and M' represents ammonium or alkali metal, in an aqueous medium of pH more than 4-less than 9.

3. Copper pyrithione aggregates produced by reaction of water-soluble metal pyrithione or ammonium pyrithione represented by general formula (I):
General Formula (I):



wherein, M represents a monovalent or bivalent metal, or ammonium, Py

represents 2-pyridylthio-N-oxide group, and $n=1$ or 2 ,
and double salt of inorganic copper (II) salt and inorganic ammonium
salt or double salt in which inorganic ammonium salt is partly replaced
by inorganic alkali metal salt represented by general formula (II):



wherein, X represents an anion selected from Cl, $1/2\text{SO}_4$ or NO_3 and M' represents ammonium or alkali metal, in an aqueous medium of pH 1-less than 9, wherein, the particle size falls within the range of 5.5-less than 9 μm by median value on the premise that the particles have a one peak pattern of distribution of particle size.

4. The copper pyrithione aggregates according to claims 1 or 3, wherein, M is a metal selected from a group consisting of sodium, potassium, calcium and magnesium.
5. The production method of the copper pyrithione aggregates according to claim 2, wherein, M is a metal selected from a group consisting of sodium, potassium, calcium and magnesium.
6. The copper pyrithione aggregates according to claims 1, 3 or 4, wherein, the inorganic copper (II) salt is copper (II) chloride or copper (II) sulfate, and the inorganic ammonium salt is ammonium chloride or ammonium sulfate, and the inorganic alkali metal salt is sodium chloride or sodium sulfate.
7. The production method of the copper pyrithione aggregates according to claims 2 or 5, wherein, the inorganic copper (II) salt is copper (II) chloride or copper (II) sulfate, and the inorganic ammonium salt is ammonium chloride or ammonium sulfate, and the inorganic alkali metal salt is sodium chloride or sodium sulfate.
8. The copper pyrithione aggregates according to claim 3, wherein, median value of particles of the copper pyrithione aggregates falls within the range of 5.5-less than 9 μm on the premise of using fine powder grinding machine.
9. An antifoulant for use in water which contains the copper pyrithione aggregates according to claim 1.
10. An antifoulant for use in water which contains the copper pyrithione aggregates according to claims 3 or 8.
11. An antifoulant for use in water according to claims 9 or 10 which is used

for ship-bottom paint or fish-farming net.