

DESCRIPTION

COPPER PYRITHIONE AGGREGATE AND USE OF SAME

Technical Field

5 [0001] The present invention relates to copper pyrithione aggregate and use of the same. For details, it relates to copper pyrithione aggregates produced by reacting water-soluble metal pyrithione or ammonium pyrithione, and double salt of inorganic copper(II) salt and inorganic ammonium salt in an aqueous medium of pH 1-4, and use of the same. For further details, it relates to an antifoulant for ship-bottom paint
10 wherein the particle size of the copper pyrithione aggregates produced by reacting water-soluble metal pyrithione or ammonium pyrithione, and double salt of inorganic copper (II) salt and inorganic ammonium salt in an aqueous medium of pH 1-4, falls within the range of 9-13 μ m by median value.

Background of the Invention

15 [0002] In JP3062825B, a method for production of copper pyrithione is disclosed wherein a surfactant is added in order to prevent gelation occurring in the 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 described
20 in the claims of this patent, first fine crystals of basic copper salt are precipitated before forming copper pyrithione. This is the actual phase of phenomenon called gelation. Although copper pyrithione is given by the reaction of slightly-soluble basic copper salt and pyrithione alkali metal salt, crystals of the product are small and the average particle size never exceeds 5 μ m. In addition, the basic copper salt remaining as
25 impurities in the copper pyrithione products, when formulated in the paint for

preventing ship-bottom from the marine organism fouling, can cause the gelation during storage of the paint.

In JP3532500B, a production method of copper pyrithione is disclosed wherein an aqueous solution of pyrithione metal salt and an aqueous solution of inorganic copper(II) salt are reacted under a high temperature within the range of pH 1.6 to 3.2, 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 reacting for a long time under low pH and high temperature, bispyrithione (dimer) is easy to be produced by oxidation of pyrithione acid, thus in the second step, a method is employed that the bispyrithione is thermally decomposed and at the same time, by adding inorganic copper(II) salt, the purity of copper pyrithione is increased. Therefore, in the second step, although the amount produced is limited, basic copper salt is precipitated first as described above. Because of only small amount of the basic copper salt produced, the average particle size of the copper pyrithione obtained by the production method of this patent is significantly larger than that of the copper pyrithione obtained by the production method of the above-mentioned JP3062825B, nevertheless it doesn't exceed 5 μ m as shown in the claims.

patent document 1: JP3062825B

patent document 2: JP3532500B

Disclosure of Invention

Problems to be resolved by the Invention

[0003] When copper pyrithione is formulated into ship- bottom paint, the biggest factor that influences its antifouling effect is leaching rate into seawater, that is, solubility in water, which depends on the surface area of the particles. It is considered that the

average particle size of the copper pyrrhithione obtained by JP3062825B is suited for the cold marine waters, and the average particle size of the copper pyrrhithione obtained by JP3532500B is suited for the mild marine waters. However, in the tropical marine waters, even the copper pyrrhithione obtained by JP3532500B is assumed to elute too rapidly into seawater, therefore in order to retard the elution into seawater much more, the development of copper pyrrhithione having a furthermore larger average particle size is expected. In addition, existing copper pyrrhithione products tend to cause dusting at the work site, and have been shown to be injurious to health when once inhaled into the lungs because of their acicular crystals.

Means of Solving the Problems

[0004] The present inventor has found a production method in which small particles of copper pyrrhithione are aggregated, and succeeded to simultaneously resolve the above-mentioned two problems by making copper pyrrhithione into granular aggregates having an average particle size of 9-13 μ m.

That is, the present invention provides;

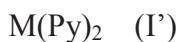
(1) Copper pyrrhithione aggregates produced by reacting water-soluble metal pyrrhithione or ammonium pyrrhithione represented by general formula (I):

[Chemical Formula 1]



or general formula (I'):

[Chemical Formula 2]



wherein, M represents a monovalent or bivalent metal, or an ammonium, Py represents 2-pyridylthio-N-oxide group, and double salt of inorganic copper(II) salt and inorganic

ammonium salt represented by general formula (II):

[Chemical Formula 3]



wherein, X represents an anion selected from any one of Cl, $1/2\text{SO}_4$ or NO_3 ,

5 in an aqueous medium of pH 1-4.

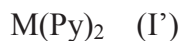
(2) Production method of copper pyrithione aggregates, characterized by being produced by reacting water-soluble metal pyrithione or ammonium pyrithione represented by general formula (I):

[Chemical Formula 4]



or general formula (I'):

[Chemical Formula 5]



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

15 2-pyridylthio-N-oxide group, and double salt of inorganic copper(II) salt and inorganic ammonium salt represented by general formula (II):

[Chemical Formula 6]



wherein, X represents an anion selected from any one of Cl, $1/2\text{SO}_4$ or NO_3 ,

20 in an aqueous medium of pH 1-4.

(3) The copper pyrithione aggregates according to the above-mentioned (1), wherein M is a metal selected from the group consisting of sodium, potassium, calcium and magnesium.

(4) The production method of copper pyrithione aggregates according to the above-mentioned (2), wherein M is a metal selected from the group consisting of sodium,

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potassium, calcium and magnesium.

(5) The copper pyrithione aggregates according to the above-mentioned (1) or (3), 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.

5 (6) The production method of copper pyrithione aggregates according to the above-mentioned (2) 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.

10 (7) The copper pyrithione aggregates according to the above-mentioned (1), (3) or (5), wherein median value of particles of the copper pyrithione aggregates is within the range of 9-13 μ m under a prerequisite that main part of particle size distribution shows a normal distribution.

15 (8) The production method of copper pyrithione aggregates according to the above-mentioned (2), (4) or (6), wherein median value of particles of the copper pyrithione aggregates is within the range of 9-13 μ m under a prerequisite that main part of particle size distribution shows a normal distribution.

(9) An antifoulant for ship-bottom paints comprising the copper pyrithione aggregates according to the above-mentioned (1).

20 (10) The antifoulant for ship-bottom paints according to the above-mentioned (9), wherein the median value of particles of the copper pyrithione aggregates is within the range of 9-13 μ m under a prerequisite that main part of particle size distribution shows a normal distribution.

[0005] M represents a monovalent or bivalent metal. For example, the monovalent metal includes sodium and potassium, and the bivalent metal includes calcium and
25 magnesium. Preferred is monovalent sodium.

[0006] As the inorganic copper(II) salt used in the production of the copper pyrrhione granular aggregates of the present invention, copper(II) chloride or copper(II) sulfate are exemplified, and the inorganic ammonium salt used in the production of the copper pyrrhione granular aggregates of the present invention includes ammonium chloride or ammonium sulfate. As the double salt of inorganic copper(II) salt and inorganic ammonium salt used in the production of the copper pyrrhione granular aggregates of the present invention, double salt of copper chloride and ammonium chloride (for example $\text{CuCl}_2 \cdot 2(\text{NH}_4)\text{Cl}$), double salt of copper sulfate and ammonium sulfate (for example $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$), double salt of cupric nitrate and ammonium nitrate (for example $\text{Cu}(\text{NO}_3)_2 \cdot 2(\text{NH}_4)\text{NO}_3$) and hydrates of these double salts are exemplified. Preferably, double salt of copper chloride and ammonium chloride (for example $\text{CuCl}_2 \cdot 2(\text{NH}_4)\text{Cl}$), double salt of copper sulfate and ammonium sulfate (for example $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$) and hydrates of these double salts are included. For example, $\text{CuCl}_2 \cdot 2(\text{NH}_4)\text{Cl} \cdot 2\text{H}_2\text{O}$ that is available commercially as dye fixatives can be used, or crystals obtained by concentrating a hydrochloric acid acidic aqueous solution of calculated amount of copper(II) chloride and ammonium chloride may be used. Similarly by concentrating a sulfuric acid acidic solution of calculated amount of copper(II) sulfate and ammonium sulfate, blue crystals of $\text{CuSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ can be obtained. Or effectively, without taking out the crystals from the above-mentioned concentrated solution, as it is as aqueous solution of production raw material for the copper pyrrhione granular aggregates of the present invention, it may be subjected to the reaction with pyrrhione metal salt aqueous solution.

[0007] In the double salt, the used amount of inorganic copper salt and inorganic ammonium salt is 1:2 by molar ratio, and the used amount of double salt and sodium pyrrhione is 1:2 by molar ratio. The formation of double salt of inorganic copper(II)

salt and inorganic ammonium salt, and the reaction of inorganic copper(II)-ammonium double salt and pyrrhione metal salt of the present invention can be suitably carried out within the range of pH 1-4. Further, as the reaction temperature, room temperature of 10-30°C is suitable. When the reaction temperature is much higher, primary particles of copper pyrrhione become too elongated to form aggregates. Since the aggregate after reaction according to the method of the present invention forms granular aggregate having average particle size of several 100µm, its filtration operation is much easier compared to conventional copper pyrrhione.

When the aggregate is pulverized to have the average particle size of less than 9µm, single particles of 0.1-1.0µm are easy to be produced in an unignorable amount, which is easy to affect the leaching behavior of the copper pyrrhione aggregates of the present invention in seawater. In addition, when pulverized to the average particle size of over 13µm, there is a possibility that the ratio of the coarse particles of more than 50µm becomes more than 10%, which might affect the coating film performance of the paint. Therefore, it is appropriate to pulverize this to the average particle size of 9-13µm (Figure 1 and Figure 6), and to use as an antifoulant for ship-bottom paints. When the average particle size is within the range of 9-13µm, the particle size distribution shows a normal distribution in the main part, thus this normal distribution becomes a prerequisite for determining the median value. This aggregate is pulverized to the average particle size of 9-13µm (Figure 1), which is used as an antifoulant for ship-bottom paints.

[0008] The granular aggregates of the present invention (average particle size about 10µm) are dispersed in water, and heated at 80°C for 30 minutes, then slight ammonia odor is generated, and about several 10% of the aggregates are decomposed. From this, the possibility is considered that the substance of the aggregate is a complex of copper

pyrithione and inorganic ammonium salt. On the other hand, in the scanning electron micrograph of the aggregate (Figure 2 and 3), only the form of copper pyrithione is recognized, further in the chart of X-ray diffraction analysis (Figure 4 and 5), only the same peak as that of conventional copper pyrithione is recognized. Judging by considering all the above findings together, the substance of the aggregate of the present invention is inferred to be a complex of copper pyrithione and a small amount of inorganic ammonium salt. That is, in the reaction, most of the dissociated inorganic ammonium salt are dissolved in the reaction solution, and removed by washing with water.

[0009] Until now, when copper pyrithione is treated in powder form, there have been concerns about damaging the health owing to inhalation by dusting caused at the work site. In particular, the point that copper pyrithione is relatively hard acicular crystals is concerned, and a method for making the particles coarse, a method for coating with resinous materials, and the like have been proposed. Although these methods are effective, cost increases are unavoidable. Since in the granular aggregates of the present invention, the particles are large, and flowable, not only the dusting is not easily to occur, but also there is no problem due to the acicular crystals. Therefore the extra treatments like the above are not needed, and the risk of health damage is greatly reduced than before, even if treated in powder form.

[0010] The leaching rate of copper pyrithione eluted from the coating film of ship-bottom paints relates to factors such as, in addition to the surface area of copper pyrithione and temperature of seawater, the nature of coating film, navigation speed of the ship, attached conditions of fouling organisms and the like. Although simply only by the ratio of surface area, its difference can't be discussed, the surface area of the copper pyrithione granular aggregates having median value of 9-13 μ m of the present

invention is 2 to 6 times broader than the surface area of commercially available copper pyrrhithione, as a result, the leaching rate into seawater is thought to be greatly reduced, and not only the antifouling efficacy under the condition of high water temperature such as tropical marine waters is improved, but also the discharge amount of copper pyrrhithione to ocean can be reduced, which is preferable from the viewpoint of environmental protection.

The copper pyrrhithione granular aggregates of the present invention are formulated in the paint for preventing ship- bottom fouling, of which the binder is silylacrylic resin, zinc acrylic resin, copper acryl resin and copolymeric resins thereof, and usually used in combination with cuprous oxide.

Effect of the Invention

[0011] While the conventional copper pyrrhithione is acicular crystals having median value of less than 5 μ m, the copper pyrrhithione obtained by the production method of the present invention is a granular aggregate of short and small particle, having a large median value i.e., 9-13 μ m, thus the risk of inhalation at the work site is reduced significantly, and also the elution into seawater is greatly decreased when used as antifoulants for ship- bottom paint, therefore antifouling efficacy can be improved.

Brief Description of the Drawings

[0012] [Fig. 1] is a chart showing median value of the particle of copper pyrrhithione aggregates obtained in Example 1. (laser diffraction particle size distribution analyzer, Horiba, Ltd., 'LA-920'; ultrasonic treatment: none)

[Fig. 2] is the scanning electron microscopic picture of copper pyrrhithione aggregates obtained in Example 1 (6000-fold).

[Fig. 3] is the scanning electron microscopic picture of copper pyrithione aggregates obtained in Example 1 (30000-fold).

[Fig. 4] is a chart showing X-ray diffraction pattern of copper pyrithione aggregates obtained in Example 1.

5 [Fig. 5] is a chart showing X-ray diffraction pattern of commercially available copper pyrithione powder (manufactured by Kolon Life Science, Inc.).

[Fig. 6] is a chart showing median value of the particle of copper pyrithione aggregates obtained in Example 2 (laser diffraction particle size distribution analyzer, Horiba, Ltd., 'LA-920'; ultrasonic treatment: 1 minute).

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Mode for Carrying Out the Invention

[0013] The present invention will be specifically illustrated in reference to the following Examples. The following Examples are just for exemplification, and the scope of the present invention is not limited by these.

Example 1

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[0014] To water 40mL in beaker were added copper(II) sulfate pentahydrate 3.0g and ammonium sulfate 1.5g, further pH was adjusted to 2 by adding 5% sulfuric acid thereto, thus an aqueous solution (A) of copper(II) sulfate-ammonium sulfate double salt was prepared. Then to water 50mL in beaker was added 40% aqueous solution of sodium pyrithione (specific gravity 1.20) 8.85g to prepare dilute aqueous solution (B) of sodium pyrithione. With keeping 25°C, (B) was added dropwise to (A) under stirring over 30 minutes. During this time, 5% sulfuric acid was appropriately added not to exceed pH 3. Resulting green copper pyrithione slurry was filtered, the residue was added back to water 100mL, and after stirring, filtration was carried out. These running operations were repeated 3 times, then the solid obtained was dried, and pulverized with a mortar

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to give green granules 3.6g.

The green granules were dispersed into 0.1% DEMOL N (Kao Co.) aqueous solution, and median value was measured with laser diffraction particle size distribution analyzer, Horiba, Ltd., 'LA-920'. As a result, it was 10.6 μ m (Figure 1). In addition,
5 when the ultrasonic function of this analyzer was worked for 1 minute, the median value was 9.5 μ m. The tendency of decreasing the numerical value by increase of this ultrasonic wave operating time is the same as in the case of commercially available copper pyrithione.

In order to observe the inner state of particles, photographs of 6000-fold (Figure
10 2) and 30000-fold (Figure 3) was taken using scanning electron microscope. As a result, it turned out that the inside is an aggregate of materials that seem to be oval or rod-like copper pyrithiones having the length of 0.1-1.0 μ m.

Next, in order to study the chemical component of the aggregate, X-ray diffraction analysis was carried out. As a result, from the fact that the positions of
15 peaks recognized on the charts (Figure 4 and 5) of the green granular aggregate and commercially available copper pyrithione (manufactured by Kolon Life Science, Inc.) are quite the same, it was confirmed that the substance of the green granular aggregate is copper pyrithione.

Furthermore, this copper pyrithione granular aggregate is dispersed in water, and
20 heated at 80°C for 30 minutes, then slight ammonia odor is generated, and about several 10% of the aggregate is decomposed. This indicates that water-soluble ammonia compounds are contained in the aggregates, and considering the process that copper pyrithione was formed from copper(II) sulfate·ammonium sulfate double salt and sodium pyrithione, it is assumed that at the reaction time, dissociated ammonium sulfate
25 was adsorbed on copper pyrithione, and combined the copper pyrithiones. That is, it is

considered that the complex was formed. However, since its evidence was not found on the chart of X-ray diffraction, the content of ammonium sulfate is assumed to be trace amount.

Example 2

5 [0015] To water 50mL in beaker were added ammonium chloride 0.05mole(2.7g) and copper(II) chloride dihydrate 0.025mole(4.3g) (pH3), then an aqueous solution (A) of copper(II) chloride-ammonium chloride double salt was prepared by adding 2N hydrochloric acid. A 0.05 mole aqueous solution (B) of sodium pyrrhione was prepared by adding 40% aqueous solution of sodium pyrrhione 18.6g to water 40mL in
10 another beaker. At room temperature (20°C), (B) was added dropwise to (A) with stirring over 10 minutes. During this time, by adding 2N hydrochloric acid appropriately, pH at the end point of reaction was adjusted to become 3. Further, stirring was kept for 30 minutes at room temperature. Resulting green slurry was filtered, the residue was added back to water 100mL, and after stirring for 10 minutes,
15 filtration was carried out. These running operations were repeated 3 times, then the solid obtained was dried, and pulverized with a mortar to give copper pyrrhione granular aggregates 7.6g.

In the result of measuring median value with the dispersed liquid of the green granules into 0.1% DEMOL N (Kao Co.) aqueous solution by laser diffraction particle
20 size distribution analyzer, Horiba, Ltd., 'LA-920', the median value was 12.1 μ m (Figure 6) when the ultrasonic function of this analyzer was worked for 1 minute.

Comparison Example 1

[0016] The copper pyrrhione granular aggregates obtained in Example 1 was moistened with water, and ground strongly with mortar to pulverize finely. Then,
25 median value of this was measured by a method similar to Example 2, as the result,

micronized particle aggregates having values of 5.0 μ m (ultrasonic treatment: none) and 3.3 μ m (ultrasonic treatment: for 1 minute) were obtained.

Comparison Example 2

[0017] The copper pyrrhione granular aggregates obtained in Example 2 were
5 micronized similarly to Comparison Example 1, and median value of this was measured similarly to give the values of 4.3 μ m (ultrasonic treatment: none) and 3.1 μ m (ultrasonic treatment: for 1 minute).

Example 3

[0018] About the copper pyrrhione granular aggregates obtained in Example 1,
10 Example 2, Comparison Example 1 and Comparison Example 2, solubility in water was measured.

1. Sample Preparation

Dispersion liquids dispersed each sample 0.05g in ultrapure water 250mL
respectively were stirred at room temperature for 24 hours. Then after filtered with
15 filter paper of 5C, subsequently with membrane filter having average hole diameter 0.45 μ m, a solution prepared by adding nitric acid to the filtrate to make 0.1 mole/L was subjected to the measurement.

2. Measuring Method

ICP emission spectrometric analysis (instrument; Shimazu Co., 'ICPS-2000')

20 The measured results are shown in Table 1.

[0019] [Table 1]

Table 1 Solubility in Water

Sample	Copper measured value (mg/L)	copper pyrrhione equivalent (mg/L)
copper pyrrhione aggregate of Example 1	<0.05	<0.25
copper pyrrhione aggregate of	<0.05	<0.25

Example 2		
copper pyrithione aggregate of Comparison Example 1	0.08	0.40
copper pyrithione aggregate of Comparison Example 1	0.09	0.45

From the result of Table 1, the solubility in water of copper pyrithione aggregates of Example 1 and Example 2 was $2/3 - 1/2$ of those of copper pyrithione aggregates of Comparison Example 1 and Comparison Example 2.

Example 4

5 [0020] The following components were uniformly mixed to obtain ship-bottom paint.

2:3 copolymer of methyl methacrylate and triisopropylsilyl acrylate (50% xylene solution) 36% by weight

Copper(I) oxide 32% by weight

Zinc oxide 4% by weight

10 Copper pyrithione granular aggregates of Example 2 3% by weight

Titanium dioxide 2% by weight

Red iron oxide 2% by weight

Fatty acid amide wax (20%) 2% by weight

Xylene 19% by weight

15 Total 100% by weight

At the preparation time, and further 6 months later, abnormality such as gelation was not recognized.

Industrial Applicability

[0021] Since the copper pyrithione granular aggregates of the present invention have a large particle diameter of 9-13 μ m by median value which is not obtained with conventional commercially available copper pyrithione, the leaching rate from coating film of ship-bottom paint is reduced, accordingly, it can be useful as antifoulants

exerting long term antifouling performance, in particular, in the tropical marine waters, further as antifoulants with a low release amount to the environment.

CLAIMS

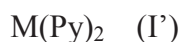
1. Copper pyrithione aggregates produced by reacting water-soluble metal pyrithione or ammonium pyrithione represented by general formula (I):

[Chemical Formula 7]



or general formula (I'):

[Chemical Formula 8]



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

10 2-pyridylthio-N-oxide group, and double salt of inorganic copper(II) salt and inorganic ammonium salt represented by general formula (II):

[Chemical Formula 9]



wherein, X represents an anion selected from any one of Cl, $1/2\text{SO}_4$ or NO_3 ,

15 in an aqueous medium of pH 1-4.

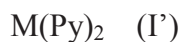
2. Production method of copper pyrithione aggregates, characterized by being produced by reacting water-soluble metal pyrithione or ammonium pyrithione represented by general formula (I):

[Chemical Formula 10]



or general formula (I'):

[Chemical Formula 11]



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

25 2-pyridylthio-N-oxide group, and double salt of inorganic copper(II) salt and inorganic

ammonium salt represented by general formula (II):

[Chemical Formula 12]



wherein, X represents an anion selected from any one of Cl, $1/2\text{SO}_4$ or NO_3 ,

5 in an aqueous medium of pH 1-4.

3. The copper pyrithione aggregates according to claim 1, wherein M is a metal selected from the group consisting of sodium, potassium, calcium and magnesium.

4. The production method of copper pyrithione aggregates according to claim 2, wherein M is a metal selected from the group consisting of sodium, potassium, calcium
10 and magnesium.

5. The copper pyrithione aggregates according to claims 1 or 3, 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.

6. The production method of copper pyrithione aggregates according to claims 2 or
15 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.

7. The copper pyrithione aggregates according claims 1, 3 or 5, wherein median value of particles of the copper pyrithione aggregates is within the range of 9-13 μm under a prerequisite that main part of particle size distribution shows a normal
20 distribution.

8. The production method of copper pyrithione aggregates according to claims 2, 4 or 6, wherein median value of particles of the copper pyrithione aggregates is within the range of 9-13 μm under a prerequisite that main part of particle size distribution shows a normal distribution.

25 9. An antifoulant for ship-bottom paints comprising the copper pyrithione

aggregates according to claim 1.

10. The antifoulant for ship-bottom paints according to claim 9, wherein the median value of particles of the copper pyrithione aggregates is within the range of 9-13 μ m under a prerequisite that main part of particle size distribution shows a normal distribution.
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