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(54) **Microbicidal composition**

Mikrobizide Zusammensetzung

Composition microbicide

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Description

[0001] This invention relates to stable microbicidal compositions containing relatively high levels of 5-chloro-2-methylisothiazolin-3-one and 2-methylisothiazolin-3-one.

[0002] A composition containing a mixture of 5-chloro-2-methylisothiazolin-3-one and 2-methylisothiazolin-3-one in a total amount of 25% by weight is disclosed in U.S. Pat. No. 5,910,503. The composition is stabilized by a metal nitrate and a metal iodate. However, there is a need for additional stabilized microbicides, especially those having higher concentrations of active ingredients and/or greater stability.

[0003] The problem addressed by this invention is to provide such additional stabilized microbicides.

STATEMENT OF THE INVENTION

[0004] The present invention is as set out in the accompanying claims.

[0005] The present invention is directed to a microbicidal composition comprising: (a) 27-37% of a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one; (b) 5-27% of a metal nitrate; (c) 30-55% water; and (d) 8-13% magnesium chloride; wherein the composition is substantially free of bromic acid, iodic acid, periodic acid or their salts.

DETAILED DESCRIPTION OF THE INVENTION

[0006] "MI" is 2-methyl-4-isothiazolin-3-one, also referred to by the name 2-methyl-3-isothiazolone. "CMI" is 5-chloro-2-methyl-4-isothiazolin-3-one, also referred to by the name 5-chloro-2-methyl-3-isothiazolone. The weight ratio of CMI to MI is at least 1:1, alternatively at least 2:1.

[0007] The weight ratio of CMI to MI is no greater than 4:1. In one preferred embodiment of the invention, the CMI:MI ratio is about 3:1.

[0008] As used herein, the following terms have the designated definitions, unless the context clearly indicates otherwise. The term "microbicide" refers to a compound capable of inhibiting the growth of or controlling the growth of microorganisms at a locus; microbicides include bactericides, fungicides and algacides. The term "microorganism" includes, for example, fungi (such as yeast and mold), bacteria and algae. The term "locus" refers to an industrial system or product subject to contamination by microorganisms. The following abbreviations are used throughout the specification: ppm = parts per million by weight (weight/weight), mL = milliliter, AI=active ingredient, i.e., total amount of isothiazolones. Unless otherwise specified, temperatures are in degrees centigrade (°C), and references to percentages (%) are by weight.

[0009] In one embodiment of the invention, the composition contains at least 28% of a mixture of CMI and MI, alternatively at least 29%, alternatively at least 30%. In one embodiment, the composition contains no more than 36% CMI/MI, alternatively no more than 35%.

[0010] A "metal nitrate" preferably is a nitrate salt of an alkali metal, an alkaline earth metal, or ammonium. Preferably, the metal is lithium, sodium, potassium, magnesium, calcium, ammonium, or a combination thereof; more preferably sodium, potassium, magnesium, or combinations thereof. Magnesium is especially preferred. Preferably, the amount of metal nitrate is at least 7%, alternatively at least 10%, alternatively at least 12%, alternatively at least 15%. Preferably, the amount of metal nitrate is no more than 25%, alternatively no more than 22%, alternatively no more than 20%, alternatively no more than 18%. A preferred metal nitrate concentration is from 7% to 27%, alternatively from 7% to 25%, alternatively from 10% to 22%. For CMI/MI concentrations at least 29%, a preferred metal nitrate concentration is from 5% to 25%, alternatively from 5% to 22%, alternatively from 7% to 22%, alternatively from 7% to 20%, alternatively from 7% to 18%.

[0011] The microbicidal composition may be prepared by adding an acidic salt of CMI/MI, preferably a hydrochloride salt, to a solution of the metal nitrate and then neutralizing the acidic salt with a basic oxide, or carbonate, e.g., magnesium oxide, basic magnesium carbonate ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$), sodium bicarbonate, sodium carbonate, potassium bicarbonate, potassium carbonate, calcium oxide and calcium carbonate. Magnesium oxide is especially preferred. Addition of metal nitrate prior to neutralization is a suitable method for producing aqueous CMI/MI compositions over a broad range of concentrations, even those outside the scope of the present invention.

[0012] The microbicidal composition may be prepared by combining the free base forms of CMI and MI (available as Technical Grade CMI/MI) with a metal nitrate. In such methods, preferably the metal nitrate content of the composition is at least 15%, alternatively at least 18%, alternatively at least 19%, alternatively at least 20%. This method is especially suitable for preparing higher concentrations of CMI/MI

[0013] The composition further comprises 8% to 13% magnesium chloride; alternatively 9% to 12%. The chloride salts may be added or generated by neutralization of CMI/MI hydrochlorides.

[0014] In one embodiment, the composition further comprises a copper salt as a stabilizer. Preferred copper salts are

copper nitrate and copper sulfate, in amounts from 1 to 200 ppm of copper.

[0015] The composition comprises 30% to 55% water. Preferably, the amount of water is no more than 50%, alternatively no more than 45%. Preferably, the amount of water is at least 35%, alternatively at least 38%.

[0016] The composition is substantially free of bromic acid, iodic acid, periodic acid or their salts, i.e., the composition contains less than 0.01% of these substances, alternatively less than 0.005%, alternatively less than 0.001%.

[0017] The microbicidal compositions of the present invention can be used to inhibit the growth of microorganisms or higher forms of aquatic life (such as protozoans, invertebrates, bryozoans, dinoflagellates, crustaceans, mollusks, etc) by introducing a microbicidally effective amount of the compositions onto, into, or at a locus subject to microbial attack. Suitable loci include, for example: industrial process water; electrocoat deposition systems; cooling towers; air washers; gas scrubbers; mineral slurries; wastewater treatment; ornamental fountains; reverse osmosis filtration; ultrafiltration; ballast water; evaporative condensers; heat exchangers; pulp and paper processing fluids and additives; starch; plastics; emulsions; dispersions; paints; latices; coatings, such as varnishes; construction products, such as mastics, caulks, and sealants; construction adhesives, such as ceramic adhesives, carpet backing adhesives, and laminating adhesives; industrial or consumer adhesives; photographic chemicals; printing fluids; household products, such as bathroom and kitchen cleaners; cosmetics; toiletries; shampoos; soaps; detergents; industrial cleaners; floor polishes; laundry rinse water; metalworking fluids; conveyor lubricants; hydraulic fluids; leather and leather products; textiles; textile products; wood and wood products, such as plywood, chipboard, flakeboard, laminated beams, oriented strandboard, hardboard, and particleboard; petroleum processing fluids; fuel; oilfield fluids, such as injection water, fracture fluids, and drilling muds; agriculture adjuvant preservation; surfactant preservation; medical devices; diagnostic reagent preservation; food preservation, such as plastic or paper food wrap; food, beverage, and industrial process pasteurizers; toilet bowls; recreational water; pools; and spas.

EXAMPLES

Example 1: Preparation of 30% Aqueous CMI/MI Solution From the Hydrochloride Salt

[0018] Into a 100mL jacketed kettle equipped with a magnetic spinbar, pH probe, thermocouple, screw-feed addition funnel and water-cooled condenser, was placed 46.3g of 40% aqueous magnesium nitrate, 7.3g water and the hydrochloride salt of a CMI/MI mixture (35g, 0.197mol). The slurry was neutralized to pH 2.0 with magnesium oxide, keeping the temperature between 25° - 30°C.

[0019] The neutralized solution was heat treated at 60°C for 3 hours, cooled and filtered to give 87.1g of product.

Storage Stability

[0020] Samples prepared by the method described above were divided into 0.5 oz (15 mL) vials and stored at 55°C for 4 weeks. Samples were taken at 4 weeks and analyzed for % of the original CMI/MI remaining (AI rem.). Results are tabulated below, along with initial CMI/MI content of the formulation (%AI_i), % Mg(NO₃)₂ (%MN), % MgCl₂ in the formulation based on MgO used (%MC), % water determined by difference.

Example	%AI _i	% MN	%MC	%H ₂ O	AI rem.
1	34.91	18.05	11.64	35.4	98.3
2	34.65	15.73	11.64	38.01	99.7
3	34.79	10.29	11.64	43.27	100
4	30.49	25.46	9.97	34.04	100
5	29.56	21.33	9.97	39.17	99.2
6	29.52	20.03	10.35	40.13	100 ^a
7	30.69	12.02	10.00	47.28	96.8
8 (Comparative)	26.83	23.3	10.00	39.87	100 ^a
9 (Comparative)	26.42	15.05	9.46	49.02	100 ^a
10 (Comparative)	25.23	24.47	8.44	41.83	100 ^a
11 (Comparative)	24.80	20.57	8.53	46.07	100 ^a
12 (Comparative)	25.25	15.03	8.50	51.25	100 ^a

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(continued)

Example	%Al _i	% MN	%MC	%H ₂ O	Al rem.
13 (Comparative)	20.23	24.48	6.72	48.55	97.8
14 (Comparative)	20.62	20.52	6.83	53.26	100 ^{a)}
15 (Comparative)	20.24	15.16	6.72	57.84	100 ^{a)}
a) results were > 100%					

[0021] All samples were clear, yellow and free of solids. Further results are tabulated below.

Example	%Al _i	% MN	%MC	% H ₂ O	Al rem.
16	31.01	17.0	10.16	41.82	98.5
17	30.25	21.9	10.16	37.72	99.4
18	30.91	12.1	10.16	46.85	97.7
19	29.64	6.5	10.16	53.66	84.9
20 (Comparative)	25.01	21.5	8.49	44.98	98.9
21 (Comparative)	24.60	16.8	8.49	50.08	100
22 (Comparative)	26.34	11.7	8.49	53.49	96.3
23 (Comparative)	24.84	6.4	8.49	60.25	5.9

Example 2: Preparation of Aqueous CMI/MI Solution from Technical Grade CMI/MI

[0022] Into a 100 mL jacketed kettle equipped with a magnetic spinbar and thermocouple was placed 50.0 g of 40% aqueous magnesium nitrate, 20.0 g of water and 30.0 g of Technical grade CMI/MI. The mixture was stirred at 25°-30°C until all of the CMI/MI dissolved. The solution was heat treated at 60°C for 3 hours, cooled and filtered to give 97.5 g of product. In some samples, magnesium chloride was added as a 30% aqueous solution. Results are presented below for samples stored for 4 weeks at 55°C. Higher %MN is required for samples prepared by this method, especially at higher %H₂O.

Example	%Al _i	% MN	%MC	%H ₂ O	Al rem.
24 (Comparative)	39.60	19.1	0	41.30	94.8
25 (Comparative)	35.07	24.1	0	40.83	100.0
26 (Comparative)	36.08	20.0	0	43.92	94.7
27 (Comparative)	34.79	10.2	0	55.01	5.7
28 (Comparative)	29.80	19.5	0	50.70	90.1
29 (Comparative)	29.75	10.3	0	59.95	4.8
30 (Comparative)	14.62	19.6	0	65.78	94.3
31 (Comparative)	32.87	25.7	0	41.39	96.1
32 (Comparative)	31.91	20.7	0	47.44	96.5
33	32.50	20.9	10.00	36.59	99.3
34 (Comparative)	32.03	16.0	0	51.96	26.1
35	31.86	15.8	10.00	42.37	100.0
36 (Comparative)	31.91	11.0	0	57.07	0.0
37	32.14	11.3	10.00	46.57	98.0

(continued)

Example	%Al _i	% MN	%MC	%H ₂ O	Al rem.
38 (Comparative)	27.78	18.1	0	54.16	96.2
39 (Comparative)	14.92	19.4	6.00	59.72	98.9

Comparative Example 1: Preparation of High-Concentration CMI/MI by Addition of Magnesium Nitrate After Neutralization

[0023] If the hydrochloride of CMI/MI is neutralized with magnesium oxide, and magnesium nitrate hexahydrate is added only after neutralization ("MN 6H₂O after") or 40% magnesium nitrate is added only after neutralization ("40% MN after"), the following solids contents are required before neutralization to achieve the indicated high concentrations. They are tabulated below for products with different %Al and %MN contents, with the % solids contents required with pre-addition of 40% MN, as in Ex. 1 ("MN before"). Mixtures with solids content above about 45% cannot be agitated well. Production of mixtures having high Al content by post-addition of MN is not feasible. In all cases, the solids content before neutralization is lower for pre-addition of 40% MN.

%Al	%MN	minimum % solids for "40% MN after"	minimum % solids for "MN 6H ₂ O after"	minimum % solids for "MN before"
35	25	NA ¹	85	46
35	20	98	73	46
35	15	76	64	46
30	25	NA ¹	72	39
30	20	83	62	39
30	15	65	54	39
25	25	93	59	33
25	20	68	51	33
25	15	53	45	33
20	25	73	47	26
20	20	53	40	26
20	15	42	35	26
1. It is not possible to prepare these Al/MN compositions with post-addition of 40% MN				

Claims

1. A microbicidal composition comprising:

- (a) 27-37% of a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl 4 isothiazolin-3-one in which the weight ratio of 5-chloro-2-methyl-4-isothiazolin-3-one to 2-methyl-4-isothiazolin-3-one is from 4:1 to 1:1;
- (b) 5-27% of a metal nitrate;
- (c) 30-55% water; and
- (d) 8-13% magnesium chloride;

wherein the composition contains less than 0.01% bromic acid, iodic acid, periodic acid or their salts.

2. The composition of claim 1 having 30-37% of a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one; and 7-22% of a metal nitrate.

Patentansprüche

1. Mikrobizide Zusammensetzung, umfassend:

- 5 (a) 27 bis 37% einer Mischung aus 5-Chlor-2-methyl-4-isothiazolin-3-on und 2-Methyl-4-isothiazolin-3-on, in welcher das Gewichtsverhältnis von 5-Chlor-2-methyl-4-isothiazolin-3-on zu 2-Methyl-4-isothiazolin-3-on von 4:1 bis 1:1 reicht,
 (b) 5 bis 27% eines Metallnitrats,
 (c) 30 bis 55% Wasser und
 10 (d) 8 bis 13% Magnesiumchlorid,

wobei die Zusammensetzung weniger als 0,01% Bromsäure, Iodsäure, Periodsäure oder deren Salze enthält.

- 15 2. Zusammensetzung nach Anspruch 1, die 30 bis 37% einer Mischung aus 5-Chlor-2-methyl-4-isothiazolin-3-on und 2-Methyl-4-isothiazolin-3-on, und 7 bis 22% eines Metallnitrats aufweist.

Revendications

20 1. Composition microbicide comprenant :

- (a) 27-37 % d'un mélange de 5-chloro-2-méthyl-4-isothiazolin-3-one et de 2-méthyl-4-isothiazolin-3-one où le rapport en poids de la 5-chloro-2-méthyl-4-isothiazolin-3-one à la 2-méthyl-4-isothiazolin-3-one est de 4:1 à 1:1 ;
 (b) 5-27 % d'un nitrate métallique ;
 25 (c) 30-55 % d'eau ; et
 (d) 8-13 % de chlorure de magnésium ;

où la composition contient moins de 0,01 % d'acide bromique, d'acide iodique, d'acide périodique ou de leurs sels.

- 30 2. Composition selon la revendication 1 ayant 30-37 % d'un mélange de 5-chloro-2-méthyl-4-isothiazolin-3-one et de 2-méthyl-4-isothiazolin-3-one ; et 7-22 % d'un nitrate métallique.

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

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