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(21) International Application Number: PCT/EP94/03629 (22) International Filing Date: 4 November 1994 (04.11.94) (30) Priority Data: P 43 38 923.6 15 November 1993 (15.11.93) DE (71) Applicant (for all designated States except US): DEGUSSA AKTIENGESELLSCHAFT [DE/DE]; Weissfrauenstrasse 9, D-60311 Frankfurt (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): SCHÄFER, Matthias [DE/DE]; Karl-Heeg-Strasse 15 b, D-63773 Goldbach (DE). DRAUZ, Karlheinz [DE/DE]; Zur Marienruhe 13, D-63579 Freigericht (DE). LOTTER, Hermann [DE/DE]; Frankfurter Strasse 40, D-63674 Altenstadt (DE).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, NO, NZ, PL, RO, RU, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: USE OF COPPER (II) METHIONINATE AS FUNGICIDE IN VITICULTURE (57) Abstract A process for the fungicidal treatment of vines by application of a formulation containing a 2-amino-4-methylmercaptobutyric acid-copper complex compound having formula (I) and the use of said compound as fungicide in viticulture. Included is also a process for the preparation of the compound having formula (I).		

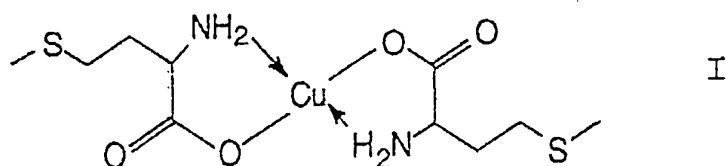
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Use of copper (II) methioninate as fungicide in viticulture

The invention relates to the use of the 2-amino-4-methylmercaptobutyric acid-copper complex compounds having formula I

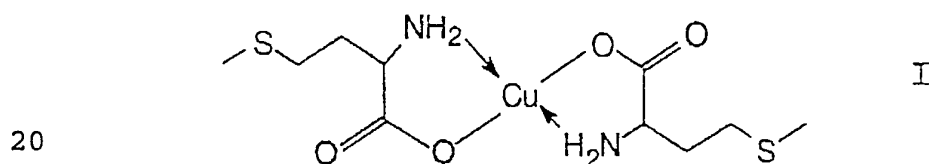


- as fungicide in viticulture, and to a process for the preparation of the complex compounds and processes for applying the formulation containing active ingredient to vines.
- It has already become known that compounds having formula I have a fungicidal effect (JP 49-12028, EP 0 482 410, DD 299 695) and have plant-regulating properties (DE 22 17 896 C, EP 0 073 391 A). The compound having formula I may thus be used for controlling rice, tomato and citrus diseases (JP 49-12028). The effect, however, particularly if small quantities are applied, is not always satisfactory in every respect.

It is also known that inorganic Cu compounds (e.g. oxides, hydroxides) are used to control perenospora (plasmopara viticola) on vines (EP 0 080 226 B). The effect of said substances is not always satisfactory in every respect because large application quantities (>50 g/hl active copper) are required to control the vine disease, which means considerable ecological pollution of the area under cultivation.

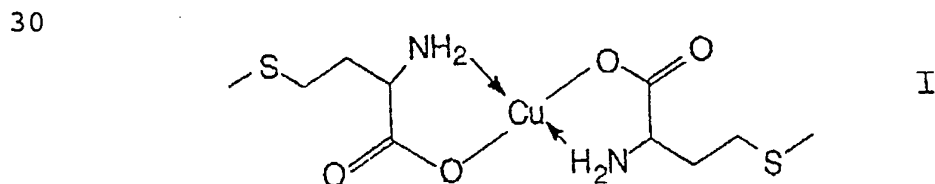
The object of the invention is to propose the use of a new fungicide in viticulture which is suitable in particular for controlling peronospora on vines. A further object is a process for the fungicidal treatment of vines and a
 5 process for the preparation of the compound having a fungicidal effect.

According to the invention, it has now been found that the compound having formula I exhibits an outstanding
 10 fungicidal effect on vines, particularly for controlling peronospora, in application quantities which are at the same time very low (<30 g/hl active copper). The invention relates, therefore, to the use of a 2-amino-4-methylmercaptobutyric acid-copper complex compound having
 15 formula I



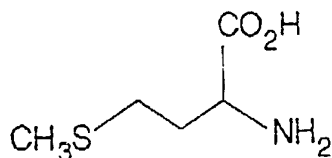
as fungicide in viticulture, particularly for the control of peronospora.

25 The invention also contains a process for the fungicidal treatment of vines by the application to vines of a composition containing a 2-amino-4-methylmercaptobutyric acid-copper complex compound having formula I



35 The invention also includes a process for the preparation of the fungicidal compounds having formula I, wherein methionine having formula II

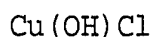
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II

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is reacted with copper oxychloride or the hydrates thereof having formula III



III

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in the presence of a diluent. The diluents considered in preference are protonic polar solvents. These include in, particular, water and alcohols such as methanol, ethanol and propanol, and mixtures thereof, optionally with other
20 solvents. Water is particularly preferred as solvent.

The reaction temperature may be varied within a relatively wide range in the process according to the invention.

Generally, operations are carried out at temperatures

25 between 0 and 100 °C, preferably between 20 and 100 °C.

The process according to the invention is generally carried out at normal pressure.

Between 0.4 and 1 mole, preferably about 0.5 mole of

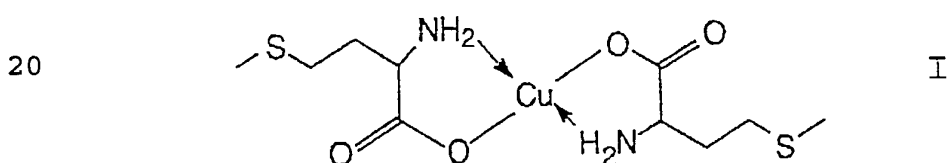
30 starting compound having formula (III) is generally used per mole of starting compound having formula (II) in order to carry out the process according to the invention. The starting substances are mixed with the diluent and optionally stirred at elevated temperature until the end of
35 the reaction. Work-up is carried out according to customary methods. The procedure is generally such that the still hot reaction mixture is cooled and adjusted with an acid acceptor to a pH of between pH 4 and pH 8,

preferably to pH 6 - pH 7. The bases used are preferably inorganic bases, for example, inorganic bases such as sodium hydroxide or potassium hydroxide. The product is optionally precipitated by the addition of an organic
5 diluent such as, for example, acetone, and isolated by customary means, e.g. by suction or centrifuging.

As mentioned already, compounds having formula I are characterised by a strong effect on perenospora on vines.
10

The compounds to be used according to the invention may be used as individual stereoisomers having formula I or as mixtures of said isomers.

15 The formulation to be used according to the invention is prepared by mixing a 2-amino-4-methylmercaptobutyric acid-copper complex compound having formula I



with diluents and/or surfactants.

25

The active ingredients may be converted to the customary formulations such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols, ultrafine encapsulations in polymer substances and in encapsulating
30 compounds for seed, and ULV formulations.

Said formulations are prepared in the known way, e.g. by mixing the active ingredients with diluents, i.e. liquid solvents, pressurised liquefied gases and/or solid
35 supports, optionally with the use of surfactants, i.e. emulsifiers and/or dispersing agents and/or foaming agents. If water is used as diluent, organic solvents, for example, may also be used as auxiliary solvents. The liquid

Method of preparation of D-L-Cu methioninate:

A suspension is prepared in an 800 l boiler at 20 °C from 50.0 kg (335 mole) of D,L-methionine, bas. copper chloride
5 18.3 kg (167 mole) (Cu content approx. 58%) and 500 l of water, which suspension is heated slowly, with stirring (approx. 1 h) to 90-95 °C.

A high stirring speed is required for an optimum procedure.

10 After 2 h at 90-95 °C, full cooling is applied and the batch is adjusted at 30 °C to pH 6.5 with conc. sodium hydroxide solution. Cooling is continued to approx. 15 °C and the product centrifuged.

15 The product is washed in the centrifuge with a total of 150 ml of water and dried in the drying cabinet at 60-80 °C under vacuum until the weight is constant.

Yield: 60 kg (99%)

20

Examples of formulation

Example 1: Preparation of a powder formulation

25 50 parts by weight of the amino acid metal complex compound according to the invention are mixed with
2 parts by weight of calcium lignin sulphonate,
2 parts by weight of alkyl naphthalene sulphonate,
1 part by weight of polyvinyl alcohol and 45 parts by
30 weight of attapulgate, and ground finely to a particle fineness essentially below μm . Said preparation is suspended in water and applied in a spraying process in a concentration of 0.4%.

35 Example 2: Preparation of a suspension concentrate

500 g of the amino acid complex compound according to the invention with 60 g of monoethylene glycol, 40 g of

emulsifier and 1 g of defoaming agent are made up to a volume of 995 ml with water and then ground in a suspension mill to a particle size of less than 5 μm . 5 ml of a thickener are then added, with stirring. Said preparation is suspended in water and applied in a spraying process in a concentration of 0.4%.

Biological results

10 Example 1: Comparison of effect on plasmopara viticola (perenospora viticola) on vines in a greenhouse

15 Application: Spraying process, 0.4% with a single application 4 h before artificial infection

Evaluation: 10 days after application

20		Attack in %	Efficacy in %	Phyto-toxicity in %
25	Agent according to the invention	0.22	99.7	0
	Comparative agent (50 g Cu/hl)	1.50	97.7	0
30	Control (untreated)	64.60	-	0

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Example 2: Comparison of effect on plasmopara viticola
(perenospora viticola) on vines in the open

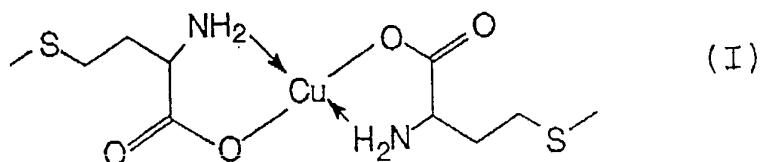
5 Application: Spraying method 0.4% with 5 applications as
from 7.6. at approx. 14 day intervals

Evaluation: 3 weeks after the final application

10	Attack in %		Phyto- toxicity in %
	Leaves	Grapes	
15			
	Agent according to the invention		0
	Comparative agent (50 g Cu/hl)		0
20	Control (untreated)		0
25			

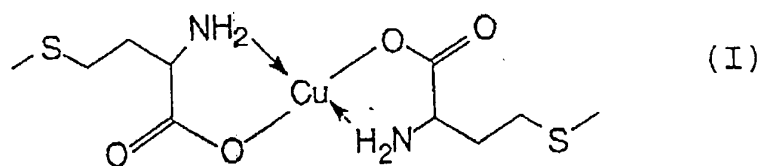
Patent claims

1. Use of a 2-amino-4-methylmercaptobutyric acid-copper complex compound having formula I



10 as fungicide in viticulture.

2. A process for the fungicidal treatment of vines, characterised in that an agent containing a 2-amino-4-methylmercaptobutyric acid-copper complex compound having formula I

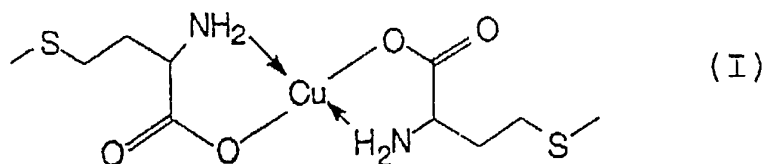


20 is applied to vines.

- 25 3. Use according to claim 1 for controlling perenospora.
4. A process according to claim 2, characterised in that it is used to control perenospora.
- 30 5. A process according to claim 2 and 4, characterised in that the formulation contains the active ingredient and diluent and/or surfactants.
- 35 6. A process according to claim 2, in which the formulation is applied in quantities such that 0.01 kg/ha to 10 kg/ha of active ingredient are applied.

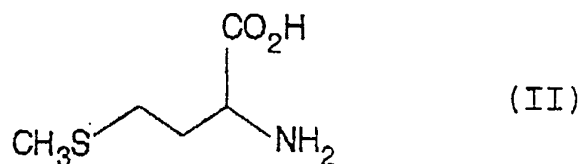
7. A process for the preparation of a 2-amino-4-methylmercaptobutyric acid-copper complex compound having formula I

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- 10 characterised in that methionine having formula II

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is reacted with copper oxychloride or the hydrates thereof having formula III

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in the presence of a diluent.

8. A process according to claim 7, characterised in that water or an alcohol is used as diluent.
9. A process according to claim 7 or 8, characterised in that the reaction is carried out in the diluent at least for part of the time at a temperature above 50 °C, particularly above 80 °C.
10. A process according to one of claims 7 to 9, characterised in that the reaction mixture is adjusted to a pH of 4 to 8, particularly at a temperature of 0 to 45 °C.