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3,279,981

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QUATERNARY AMMONIUM IODIDE FOR COMBATING PHYTOPATHOGENIC MICROORGANISMS

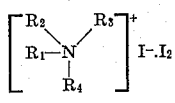
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Claims priority, application Switzerland, May 30, 1963, 6,817/63
7 Claims. (Cl. 167—22)

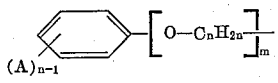
The present invention provides a preparation for combating phytopathogenic microorganisms, which comprises, as active substance, a reaction product of (a) a quaternary ammonium compound with (b) a compound of iodine with an iodide, preferably $Me^+[I_3]^-$—wherein Me^+ represents a sodium or preferably a potassium ion in the molecular ratio of approximately $a:b=1:1$, together with a suitable carrier.

In the preparations of the inevention, one or more of the following additives may be present: a vehicle, a solvent, a dispersant, an adhesive, a fertilizer and a further pesticide.

The present invention provides especially a preparation for combating phytopathogenic microorganisms, comprising as active substance a compound of one of the following general formulae:

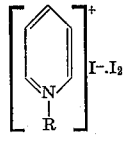


wherein R_1 represents an alkyl radical containing 1 to 18 carbon atoms, or the radical having the formula



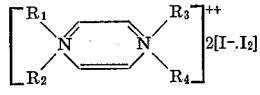
wherein A represents an alkyl radical containing 1 to 18 carbon atmos and n and m each represents a whole number from 1 to 4; R_2 and R_3 each represents an alkyl or hydroxyalkyl radical containing 1 to 18 carbon atoms, and R_4 represents an alkyl or hydroxyalkyl radical containing 1 to 18 carbon atoms or an arylalkyl radical, preferably the benzyl radical;

(b)



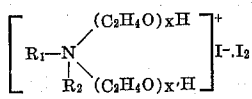
wherein R represents an alkyl radical containing 1 to 18 carbon atoms or an arylalkyl radical, preferably the benzyl radical;

(c)



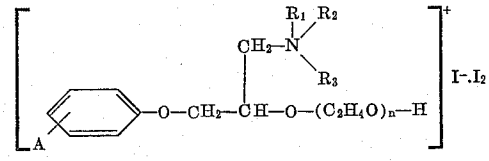
wherein R_1 to R_4 each represents a lower alkyl radical, preferably the methyl radical;

(d)



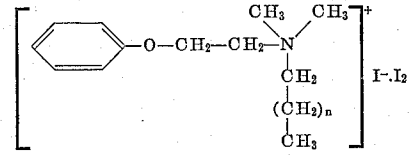
wherein R_1 represents an alkyl radical containing 1 to 18 carbon atoms and R_2 represents a lower alkyl radical, and X and X' together represent a value not exceeding 50;

(e)



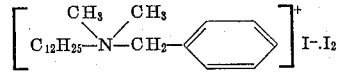
wherein A represents an alkyl radical containing 1 to 18 carbon atoms, R_1, R_2 and R_3 each represents a lower alkyl radical, and n is a whole number not exceeding 50;

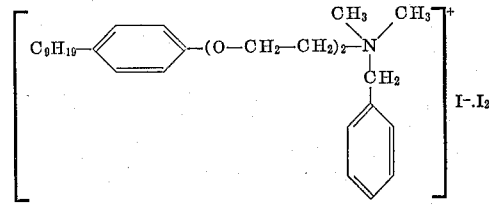
(f)

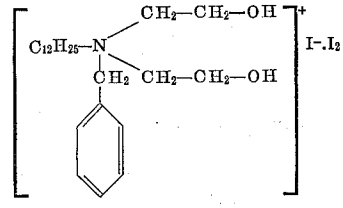


wherein n is a whole number from 6 to 10, preferably 10.

An especially favorable effect is obtained when using as active substance one of the following compounds







The compounds of the above formulae can be prepared by mixing the above ingredents (a) and (b) in an aqueous solution in the approximate molecular ratio of a $a:b=1:1$. The isolation of the reaction product from the reaction mixture is, in most cases, facilitated by the lesser solubility of the former.

The new preparations are above all potent fungicides, for example, they are especially suitable for combating leaf spot fungi on plants.

Furthermore, mention should be made of the effect of the new compounds against phytopathogenic bacteria

The present invention further includes a method of combating phytopathogenic microorganisms, wherein a microbicidal amount of one of the compounds defined above is applied to the plants, plant seed or seedlings to be protected and/or to the soil in which the plant seeds or seedlings are to be planted.

The present invention further includes the compounds of the above compositions as such, insofar as they are new.

Of special significance is the fact that the active substances to be used according to the invention, when applied in a concentration necessary to achieve parasite control, do practically no damage to the plants treated with them.

The excellent effect of the active substances of the invention against the said phytopathogenic microorganisms could certainly not have been foreseen.

In view of the very distinct differentiation in the lower plant kingdom it is, as is known, impossible to make deductions from the known action on a certain type of microorganisms, for example bacteria, that infest the skin, concerning genetically and oecologically differently constituted microorganisms, for example, phytopathogenic fungi.

More especially, it could not have been expected that the active substances used in the invention, notwithstanding their very strong effect upon the aforementioned harmful microorganisms, would not harm the higher plants treated. It is known that quaternary active substances very often harm higher plants causing, for example, burning of leaves, and this danger is particularly evident in the case of very potent compounds. The expert would certainly have expected that by using quaternary compounds such as those used according to this invention, damage, especially burning of leaves, would occur on delicate culture plants.

Thus, the excellent effect of the compounds to be used in the invention upon the said phytopathogenic microorganisms without damaging the plants treated is certainly unexpected, more especially also in view of the fact that combinations of nonionic surface-active compounds with iodine/iodide complexes display strong phytotoxic side effects when used to combat phytopathogenic microorganisms.

The preparations of the invention containing the compounds of the above formulae as active substances may be used in a variety of forms of application, for example pastes, powders, emulsions, suspensions, solutions or sprays.

For the manufacture of liquids suitable for direct spraying there may be used, for example, petroleum fractions of a high to medium boiling range, preferably above 100° C., for example Diesel oil or kerosene, also coal tar oils and oils of vegetable or animal origin, as well as hydrocarbons for example alkylated naphthalenes and tetrahydronaphthalene, if desired in admixture with xylene mixtures, cyclohexanol, ketones, also chlorinated hydrocarbons for example tetrachloroethane, trichloroethylene or tri- and tetrachlorobenzenes.

Aqueous forms of application of the active substances to be used according to the invention are obtained by dissolution of the preparation in water, or from pastes or wettable spray powders by addition of water. Suitable emulsifiers or dispersants are, for example, nonionic products, for example ethylene oxide condensation products of aliphatic alcohols, amines or carboxylic acids having a long-chain hydrocarbon radical of about 10 to 20 carbon atoms, for example the condensation products of octadecyl alcohol with 25 to 30 mols of ethylene oxide, or of soyabean fatty acid with 30 mols of ethylene oxide, or of commercial oleylamine with 15 mols of ethylene oxide, or of dodecylmercaptan with 12 mols of ethylene oxide. Suitable cationic dispersants are, for example, quaternary ammonium compounds for example cetyl pyridinium bromide or dihydroxyethyl benzyl dodecyl ammonium chloride. There may also be used anionic emulsifiers, preferably in conjunction with nonionic emulsifiers and/or organic solvents.

For the manufacture of dusting and scattering preparations there may be used as solid vehicle: talcum, kaolin, bentonite, calcium carbonate, calcium phosphate, or coal, cork meal, wood meal or other materals of vegetable origin.

The preparations of the invention may be used by themselves or in conjunction with conventional pesticides, more especially insecticides, acaricides, nematocides, selective herbicides or further fungicides and bactericides.

The preparations of the invention may contain the usual additions of substances that improve the distribution, adhesion, stability towards rain or the penetration; as such substances there may be mentioned fatty acids, resins, glue, casein and alginates.

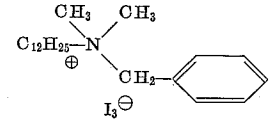
As pesticides that may be present in the preparations of the invention in addition to the compounds of the above formulae there may be mentioned, for example, 3,4-dichlorobenzyl alcohol, halogenated dihydroxydiphenylmethanes, tetramethyl-thiuram disulfides, 2,2'-thio-bis-(4-dichloro-phenol), 2-nitro-2-furfuryl iodide, salicyl anilides, dichlorosalicyl anilides, dibromosalicyl anilides, tribromosalicyl anilide, dichlorocyanuric acid, tetrachlorosalicyl anilides, aliphatic thiuram sulphides and "hexachlorophene" (2,2'-dihydroxy-3,5,6-3',5',6'-hexachlorodiphenylmethane).

The following examples illustrate the invention, the percentages being by weight.

Example 1

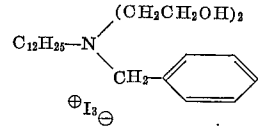
(a) 500 g. of iodine were mixed with 327 g. of potassium iodide (molecular ratio 1:1). 50 g. of water were then stirred in, and everything passed into solution. The resulting equimolecular iodine-iodide solution, which contained the compound $K^+[I_3]^-$, was then diluted with a further 123 g. of water.

(b) 67.8 g. (0.2 mol) of dodecyl benzyl dimethyl ammonium chloride were dissolved in 250 cc. of water. While stirring the solution well, 102 g. (0.2 mol) of the iodine-iodide solution obtained as described under (a) were then rapidly run in. The reaction product solidified; it was comminuted in a mortar and thoroughly washed with water. The crude product was recrystallized from alcohol, to yield brown crystalline flakes melting at 68 to 72° C. of the formula



Analysis.—I_2 content—calculated 37%, found 37.6%.

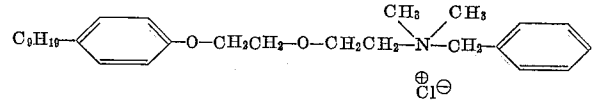
(c) 75 g. (0.2 mol) of dodecyl benzyl dihydroxyethyl ammonium chloride were dissolved in 250 cc. of water. While stirring the solution well, 102 g. (0.2) of the iodine-iodide solution obtained as described under (a) were rapidly run in. A rather mobile, dark brown substance was obtained which was repeatedly kneaded with water and the supernatant liquid decanted. The reaction product of the formula



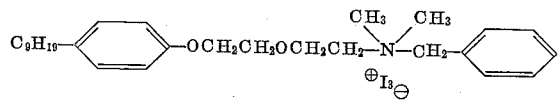
was dried in air.

Analysis.—Iodine content—calculated 34.9%, found 33.0%.

(d) 89.5 g. (0.2 mol) of the compound of the formula



were dissolved in 270 cc. of water. While thoroughly stirring the solution, 102 g. (0.2 mol) of the iodine-iodide solution prepared as described under (a) were rapidly run in, to form a little mobile, tough, dark paste which was repeatedly kneaded with water and the supernatant liquid decanted. The reaction product of the formula



was dried in air.

Analysis.—Iodine content—calculated 32.0%, found 32.7%.

(e) Method of determining the content of elemental iodine (I_2): 0.5 to 1 g. of the reaction products obtained in Example 1(b) to (d) was dissolved in 20 to 50 cc. of benzene, and the elemental iodine was titrated and well stirred with 0.1 N-thiosulphate solution until the brown coloration disappeared.

Example 2

(a) 6 g. of the reaction product obtained under 1(b) and 3 g. of an emulsifier consisting of a mixture of a nonionic and an anionic surface-active substance (registered trademark "Toximul L") were diluted with xylene to 30 cc. The resulting clear solution could be diluted with water in any desired proportion to form an emulsion ready for use as a spray broth.

(b) As described under (a) above, 6 g. of the reaction product from 1(e) and 6 g. of an emulsifier consisting of a mixture of a nonionic and an anionic surface-active substance ("Toximul S," registered trademark) were diluted with xylene to 30 cc.

(c) As described under (a) above, 6 g. of the reaction product from 1(d) and 6 g. of the emulsifier described under (b) above were diluted with xylene to 30 cc.

(d) A spray powder was prepared in the following manner:

10 g. of one of the active substances used in Example 1 under (b), (c) and (d) were dissolved in 60 g. of acetone each and mixed with 79 g. of kaolin, and the acetone was then evaporated. The residue was mixed with the following additives; 1 g. of an emulsifier consisting of a condensation product of 1 mol of para-tertiary octylphenol with 8 mols of ethylene oxide; 10 g. of a condensation product of 1 mol of formaldehyde with 1 mol of naphthalenesulphonic acid.

Example 3

(A) Tomato plants were sprayed with the preparations from Example 2 shown in the following table, the concentration of active substance being as listed in the table. 2 days after spraying the tomato plants were infested with a spore suspension of *Phytophthora infestans.* After the infection the plants were kept for 2 days in an incubation chamber at 95 to 100% relative humidity at 22 to 25° C. The results were evaluated 6 to 8 days after infection and are listed in the following table:

Preparation of Example 2	Concentration of active substance, parts per million	Effect upon *Phytophthora infestans*, percent
(a)	736	90.
(b)	680	97.
(c)	630	92.
		Referred to the untreated reference plant=0% effect.

(B) The effect of the preparation of Example 2(b) on *Alternaria solani* was tested under the conditions indicated under (A) above: the effect observed was 72% (referred to the untreated reference plant=0%).

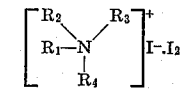
(C) The effect of the preparations of Example 2(a), (b) and (c) on *Septoria apii* on celery plants was tested under the conditions indicated under (a) above; the results are listed in the following table:

Preparation of Example 2	Concentration of active substance, parts per million	Effect of *Septoria apii* in percent
(a)	736	100.
(b)	680	100.
(c)	630	100.
		Referred to the untreated reference plant=0% effect.

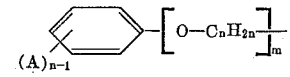
On plants treated under the conditions described under (A), (B) and (C) above, no damage or only an insignificant amount of damage was observed.

What is claimed is:

1. A method for combating phytopathogenic microorganisms without causing phytotoxic side-effects which comprises applying to an area to be protected an effective amount of a quaternary ammonium compound of the formula

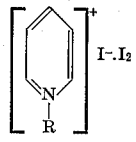


wherein R_1 represents a member selected from the group consisting of alkyl containing 1 to 18 carbon atoms, and the radical



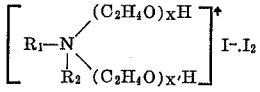
wherein A represents alkyl containing 1 to 18 carbon atoms, *n* and *m* each is a whole number from 1 to 4. R_2 and R_3 each represents a member selected from the group consisting of alkyl and hydroxyalkyl containing 1 to 18 carbon atoms, and R_4 represents a member selected from the group consisting of alkyl and hydroxyalkyl containing 1 to 18 carbon atoms and benzyl.

2. A method as claimed in claim **1**, wherein an effective amount of a compound of the formula



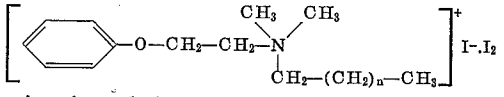
wherein R represents a member selected from the group consisting of alkyl containing 1 to 18 carbon atoms and benzyl is used.

3. A method as claimed in claim **1**, wherein an effective amount of a compound of the formula



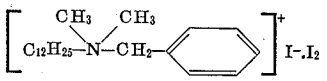
wherein R_1 represents alkyl containing 1 to 18 carbon atoms, R_2 represents lower alkyl and X and X′ together represents a value not exceeding 50, is used.

4. A method as claimed in claim **1**, wherein an effective amount of the compound of the formula



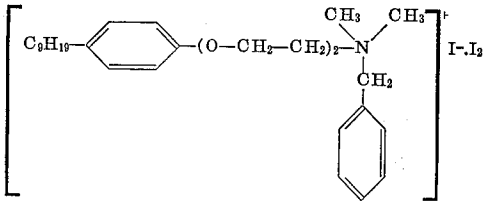
wherein *n* is a whole number from 6 to 10, is used.

5. A method as claimed in claim **1**, wherein an effective amount of the compound of the formula



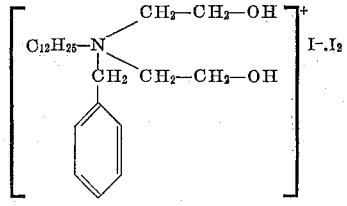
is used.

6. A method as claimed in claim **1**, wherein an effective amount of the compound of the formula



is used.

7. A method as claimed in claim **1**, wherein an effective amount of the compound of the formula



is used.

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