

PATENT SPECIFICATION

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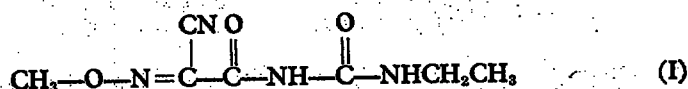


(54) IMPROVEMENTS IN OR RELATING TO FUNGICIDES

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, United States of America, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns improvements in or relating to fungicides and more particularly relates to a mixture of compounds which is useful in controlling diseases of plants. Fungi and other disease incitants cause extensive losses in crops annually. While there are commercially available materials effective in preventing many plant diseases, still further improvement in this art is needed if full food and fiber production is to be realized. The mixtures of this invention are particularly effective for the control of fungus plant diseases like potato and tomato late blight as well as the downy mildews. In addition, some of the mixtures of this invention exhibit systemic and curative properties. Relatively small amounts of each compound in the mixture can be used to eradicate or cure existing plant disease caused by fungi. This is in contrast to most conventional protective materials which must be applied in advance of attack.

One aspect of our invention provides a fungicidal mixture comprising from 1 to 10 parts by weight of



and from 1 to 1000 parts by weight of a fungicide selected from manganese ethylenebisdithiocarbamate, admixed with inorganic zinc salts; co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb); zinc ethylenebisdithiocarbamate; fixed copper; N-(trichloromethylthio)phthalimide (folpet); 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil); *cis*-N-[(1,1,2,2-tetrachloroethylthio)-4-cyclohexene-1,2-dicarboximide (captafol); and triphenyltin hydroxide.

The fungicides used together with 2-cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide may be classified as follows:

- A. manganese ethylenebisdithiocarbamate, admixed with inorganic zinc salts;
- B. co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb);
- C. zinc ethylenebisdithiocarbamate;
- D. fixed copper, such as basic copper sulfate, basic copper carbonate, copper oxychloride, and/or copper oxide;
- E. N-(trichloromethylthio)phthalimide (folpet);
- F. 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil);
- G. *cis*-N-[(1,1,2,2-tetrachloroethylthio)-4-cyclohexene-1,2-dicarboximide (captafol);
- H. triphenyltin hydroxide.

Broadly, the weight ratio of Formula I to fungicides A—H in the mixture is 10:1 to 1:1000. Application of these mixtures to the locus to be protected from

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disease effectively prevents the debility (when the fungal pathogen is sensitive to the compounds employed). Many of these mixtures are also systemic and curative in plants. Because they are curative, the mixtures can be applied before or after the plants to be protected are infected by fungi. Because the mixtures are systemic in plants, they can be applied not only directly to the infected plant parts, but also to uninfected parts of the plant or to the soil. All of these application sites are included within the term "applying to the plants".

Effective compositions of the mixtures described above comprise one of the above mixtures and an inert diluent. Surfactants can also be included as well as other ingredients which do not detract from the effectiveness of the combination.

The compound of Formula I, 2-cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide and its preparation are described and claimed in our British Patent Specification No. 1,452,256. This compound, its preparation compositions containing it and its use as a fungicide are also within the scope of the claims of our British Patent Specifications Nos. 1,425,621 and 1,425,622.

Compounds A—H are known in the art and may be prepared by conventional methods known to one skilled in the art.

Mixtures of this invention which are especially preferred are the compound of Formula I and one of the following compounds:

- A. manganese ethylenebisdithiocarbamate, admixed with inorganic zinc salts;
- B. co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb);
- D. fixed copper, such as basic copper sulfate, basic copper carbonate, copper oxychloride, and/or copper oxide;
- E. N-(trichloromethylthio)phthalimide (folpet);
- H. triphenyltin hydroxide.

Additionally, a three-component mixture of the compound of Formula I, fungicide B and fungicide D may be advantageously utilized.

Most preferred for exceptional disease control is the mixture of the compound of Formula I and the co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb).

The mixtures of this invention may contain the active ingredients, Formula I and one of fungicides A—H, in the following ratios:

Broad:	10:1 to 1:1000
Preferred:	5:1 to 1:500
Most preferred:	2:1 to 1:100.

In addition to the combinations previously named and especially useful, compositions may further contain, in addition to the two or more essential components, an agricultural chemical selected from the following list:

- bis(dimethylthiocarbamoyl)disulfide; or tetramethylthiuram disulfide (thiram);
- metal salts of ethylenebisdithiocarbamic acid or propylenebisdithiocarbamic acids, e.g. manganese, zinc, iron and sodium salts (maneb or zineb);
- n-dodecylguanidine acetate (dodine);
- N-[(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide captan];
- 2,4-dichloro-6-(o-chloroanilino)-s-triazine ("Dyrene");
- 3,3'-ethylenebis(tetrahydro-4,6-dimethyl-2H-1,3,5-thiadiazine-2-thione) (milneb);
- triphenyltin acetate (fentin acetate);
- N'-dichlorofluoromethylthio-N,N-dimethyl-N'-phenylsulfamide (dichlofluanid);
- tribasic copper sulfate;
- sulfur;
- methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate (benomyl);
- methyl 2-benzimidazolecarbamate;
- 1,2-bis(3-methoxycarbonyl-2-thioureido)benzene (methyl thiophanate);

The agricultural chemicals listed above are merely exemplary of the compounds which can be mixed with the active compounds of this invention and are not intended to any way limit the invention.

The mixtures of this invention are useful as plant disease control agents. Most have qualities of systemic and curative activity when applied to soil, to propagation pieces, to stems, or to foliage. The systemic and curative effects of the disease-control

agents of this invention make a valuable contribution to such mixtures. The systemic property of the mixtures of this case is strikingly evident in the control of potato and tomato late blight disease on the foliage when treatments with the combinations are applied solely to the root system. Additional evidence comes from the curative action against established infections by the casual agent of late blight disease. The disease can be arrested even when treatments are delayed hours after plants have been inoculated.

Of the fungi causing diseases on agricultural crops, those classed as Phycomycetes are among the most virulent. The disorders caused by this group of fungi include late blight of tomatoes and potatoes, as well as downy mildew of grapes, cole crops, legumes, and cucurbits. Diseases caused by Phycomycetes are especially susceptible to control by the mixtures of this invention.

The mixtures of this invention provide protection from damage caused by certain fungi when applied to the proper locus by the methods described hereinafter and at a sufficient rate to exert the desired effect. They are especially suited for the protection of living plants by applying the mixtures of this invention to the soil in which they are growing or in which they may subsequently be seeded or planted, to seeds, tubers, bulbs, or other plant reproductive parts prior to planting, as well as to foliage, stems, and/or fruit. Soil applications are made with dusts, granules, pellets, solutions, emulsions, or slurries.

Preferred rates for application of the active ingredients of the claimed mixtures to soil in which plants are or will be growing range from 0.5 to 500 ppm by weight of the soil in which the roots are or will be growing. More preferred use rates are in the range of 1 to 200 parts per million. The most preferred rates are in the range of 5 to 100 ppm. Preferred rates for application to seeds, tubers, bulbs, or other plant reproductive parts range from 0.5 to 100 g of active ingredients in the combinations of this invention per kilo of planting material treated. More preferred rates are in the range of 1—75 g of active ingredients per kilo. The most preferred rates are in the range of 2—50 g per kilo. Applications of this type are made with dusts, slurries, emulsions, or solutions.

Preferred rates of application for the mixtures of this invention to foliage, stems, and/or fruit of living plants range from 0.1 to 30 kilograms of active ingredients per hectare. More preferred rates are in the range of 0.2 to 20 kilos per hectare. The most preferred rates are in the range of 0.3 to 10 kilograms per hectare. The optimum amount within this range depends upon a number of variables which are well known to those skilled in the art of plant protection. The variables include, but are not limited to the disease to be controlled, weather conditions expected, the type of crop, stage of development of the crop, and the interval between applications. Applications within the range given may need to be repeated one or many more times at intervals of 1 to 60 days. Applications are made with dusts, slurries, emulsions, or solutions.

The useful mixtures can be applied in a variety of formulations, including wettable powders, water-soluble powders, suspensions, emulsifiable concentrates, dusts, solutions, granules and pellets. High strength compositions may also be prepared for use by local formulators in further processing.

These formulations include the mixtures useful in this invention, and can include surface-active agents, solid or liquid diluents and other materials as required to produce the desired formulation.

The surface-active agents act as wetting, dispersing and emulsifying agents which assist dispersion of the active material in a spray, and improve wetting of waxy foliage and the like by the spray. Thus they aid in convenience, accuracy and effectiveness in use. The surfactants can include such anionic, non-ionic and cationic agents as have been used heretofore in pesticidal compositions of similar type. A detailed list of such agents may be found in "Detergents and Emulsifiers Annual", (John W. McCutcheon, Inc.). Addition of surfactants also prevents precipitation of large crystals of the active compounds on plant surfaces and improves penetration of the active compounds, thus increasing activity. Anionic and nonionic surfactants are preferred. Such preferred surfactants include alkali and alkaline earth salts of alkylarylsulfonic acids, such as dodecylbenzenesulfonates and alkylnaphthalenesulfonates, dialkyl sodium sulfosuccinate esters, sodium lauryl sulfate, sodium N-methyl-N-oleoyltaurate, sodium dodecylphenyl ether disulfonate and the oleic acid ester of sodium isethionate. Other preferred surfactants include alkyl and alkylphenyl polyethylene glycol ethers, and their phosphate derivatives, polyoxyethylene derivatives of sorbitan fatty esters and long-chain alcohols and mercaptans, as well as polyoxyethylene esters of fatty acids. Film forming water-soluble polymers may be used in place of surfactants to improve activity. Humectants and oils chosen for low phytotoxicity also contribute to enhanced activity

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of the compositions of this invention. White oils having a viscosity of about 150 S.S.U. or higher are preferred.

Further information on formulation of the active compounds described above into the fungicidal compositions of this invention can be found in U.S. Patents Nos. 3,576,834 and 3,560,616 and E. Somers, "Formulation", Chapter 6 in Torgeson, "Fungicides", Vol. I, Academic Press, New York, 1967.

The following non-limiting examples further illustrate the invention. All parts and percentages are by weight.

EXAMPLE 1

A wettable powder can be prepared as follows:

	Percent
2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide	12
manganese ethylene bisdithiocarbamate (maneb)	78
paraformaldehyde	1
sodium ligninsulfonate	1
zinc sulfate	1
sodium alkyl naphthalene sulfonate	0.5
methyl cellulose	0.25
kaolinite	6.25

The ingredients are blended and finely ground in a hammer mill to produce a wettable powder practically all of which will pass through a U.S.S. #100 screen (0.149 mm openings).

The above formulation is dispersed in a spray tank to give a concentration of 200 ppm active 2-cyano-N-ethylcarbamoyl-2-methoxyiminoacetamide. The maneb is also an active component in this formulation. This mixture is compared with treatments of an equal amount of maneb (1300 ppm) and maneb at double that concentration (2600).

Tomato plants growing uniformly in a field are inoculated with a spore suspension of *P. infestans* during a light rain which keeps the foliage wet overnight. The field is divided into plots so that each treatment can be replicated on four different plots. Treatments are applied as a spray to run off the day after the incubation. Additional applications are made at 7 to 10 day intervals and in each case the sprays follow a natural or artificial (sprinkler) inoculation period by one or two days. By the end of the test period the untreated plants are more than 90% defoliated by late blight infections. The plants which are treated with maneb at 1300 ppm are more than 50% defoliated and those treated with maneb at 2600 ppm are about 30% defoliated. In contrast, the mixture in this formulation containing the active ingredient of this invention is so effective in curing established infections and preventing new infections that only an occasional lesion can be found in plots treated with this mixture.

The manganese ethylenebisdithiocarbamate in the above formulation can be replaced with similar amounts of commercial solid formulations of 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil); N-(trichloromethylthio)-phthalimide (folpet); cis-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclohexene-1,2-dicarboximide (captafol); zinc ethylene bisdithiocarbamate; fixed copper, such as basic copper sulfate, basic copper carbonate, copper oxychloride, and/or copper oxide; triphenyltin hydroxide; or the coordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb).

EXAMPLE 2

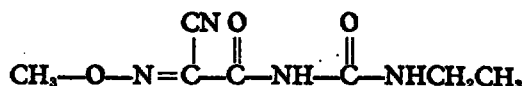
In this Example, grape vines spray treated with a mixture of this invention were healthier than comparable vines treated with either of the components of the mixture. Individual vines in a vineyard near Bordeaux, France, were treated with test materials alone or in admixture at concentrations listed in the table below. Treatments were applied on a weekly schedule starting July 7. Each treatment was applied to 10 replicate vines. Natural infection by the grape downy mildew fungus, *Plasmopora viticola*, resulted in disease on over 50 percent of the leaves of untreated vines on August 27 when all vines were rated for infection. Both of the components of the mixture reduced the disease incidence and the mixtures almost eliminated all infection.

TABLE

	Material	gm. active ingredient/ 100 liters	Percent of leaves infected by P. viticola	
5	I)	20 40 60	20 15 12	5
10	B) mancozeb	80 120 160	21 20 20	10
15	I + B)	10 15 20	160 120 80	1.8 1.8 2.5
	Untreated	—	—	58

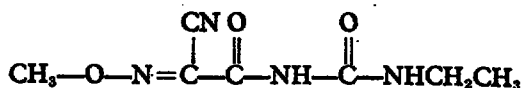
- I) 2-Cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide.
B) Co-ordination product of zinc ion and manganese ethylene bisdithiocarbamate (mancozeb).

20 WHAT WE CLAIM IS: — 20
1. A fungicidal mixture comprising from 1 to 10 parts by weight of



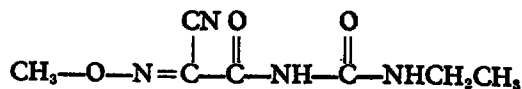
25 and from 1 to 1000 parts by weight of a fungicide selected from manganese ethylene- 25
bisdithiocarbamate, admixed with inorganic zinc salts; co-ordination product of zinc
ion and manganese ethylenebisdithiocarbamate (mancozeb); zinc ethylene bisdithio-
carbamate; fixed copper; N-(trichloromethylthio)phthalimide (folpet); 2,4,5,6-tetra-
chloroisophthalonitrile (chlorothalonil); *cis*-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclo-
hexene-1,2-dicarboximide (captafol); and triphenyltin hydroxide.

30 2. A fungicidal mixture according to claim 1 comprising from 1 to 10 parts by 30
weight of



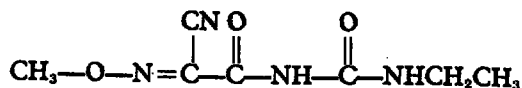
35 and from 1 to 1000 parts by weight of a fungicide selected from manganese ethylene-
bisdithiocarbamate, admixed with inorganic zinc salts; co-ordination product of zinc
ion and manganese ethylenebisdithiocarbamate (mancozeb); fixed copper; N-trichloro-
methylthio)phthalimide (folpet); and triphenyltin hydroxide. 35

3. A fungicidal mixture comprising from 1 to 10 parts by weight of



40 and from 1 to 1000 parts by weight of co-ordination product of zinc ion and manganese 40
ethylenebisdithiocarbamate (mancozeb).

4. A fungicidal mixture comprising from 1 to 10 parts by weight of



and from 1 to 1000 parts by weight, in total, of co-ordination product of zinc ion and
manganese ethylenebisdithiocarbamate (mancozeb), and fixed copper.

5. A fungicidal mixture according to claim 1, 2 or 4 wherein said fixed copper

TABLE

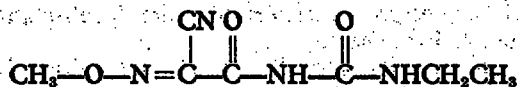
Material	gm. active ingredient/100 liters	Percent of leaves infected by <i>P. viticola</i>
I)	20	20
	40	15
	60	12
B)		
mancozeb	80	21
	120	20
	160	20
I+B)	10	1.8
	15	1.8
	20	2.5
Untreated	—	58

I) 2-Cyano-N-(ethylcarbamoyl)-2-methoxyiminoacetamide.

B) Co-ordination product of zinc ion and manganese ethylene bisdithiocarbamate (mancozeb).

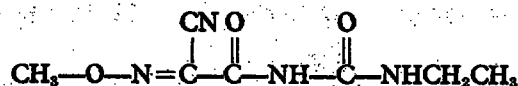
WHAT WE CLAIM IS:—

1. A fungicidal mixture comprising from 1 to 10 parts by weight of



and from 1 to 1000 parts by weight of a fungicide selected from manganese ethylene-bisdithiocarbamate, admixed with inorganic zinc salts; co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb); zinc ethylene bisdithiocarbamate; fixed copper; N-(trichloromethylthio)phthalimide (folpet); 2,4,5,6-tetrachloroisophthalonitrile (chlorothalonil); *cis*-N-[(1,1,2,2-tetrachloroethyl)thio]-4-cyclohexene-1,2-dicarboximide (captafol); and triphenyltin hydroxide.

2. A fungicidal mixture according to claim 1 comprising from 1 to 10 parts by weight of



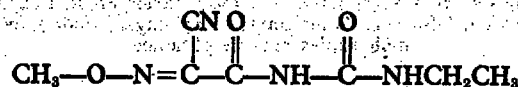
and from 1 to 1000 parts by weight of a fungicide selected from manganese ethylene-bisdithiocarbamate, admixed with inorganic zinc salts; co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb); fixed copper; N-trichloromethylthio)phthalimide (folpet); and triphenyltin hydroxide.

3. A fungicidal mixture comprising from 1 to 10 parts by weight of



and from 1 to 1000 parts by weight of co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb).

4. A fungicidal mixture comprising from 1 to 10 parts by weight of



and from 1 to 1000 parts by weight, in total, of co-ordination product of zinc ion and manganese ethylenebisdithiocarbamate (mancozeb), and fixed copper.

5. A fungicidal mixture according to claim 1, 2 or 4 wherein said fixed copper



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is basic copper sulfate, basic copper carbonate, copper oxychloride and/or copper oxide.

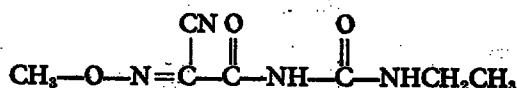
6. A fungicidal composition comprising a mixture according to any of claims 1—5 and at least one of (a) a surface-active agent and (b) a solid or liquid diluent.

7. A fungicidal composition comprising a mixture according to claim 2 and at least one of (a) a surface-active agent and (b) a solid or liquid diluent.

8. A fungicidal composition comprising a mixture according to claim 3 and at least one of (a) a surface-active agent and (b) a solid or liquid diluent.

9. A fungicidal composition comprising a mixture according to claim 4 and at least one of (a) a surface-active agent and (b) a solid or liquid diluent.

10. A fungicidal composition according to any of claims 6—9 wherein the weight ratio of



to said other fungicide is in the range 5:1 to 1:500.

11. A fungicidal composition according to claim 10 wherein the weight ratio of



to said other fungicide is in the range 2:1 to 1:100.

12. A fungicidal composition according to any of claims 6—11 including an agricultural chemical selected from the list herein.

13. A fungicidal composition according to claim 1 substantially as hereinbefore described with reference to Example 1.

14. A fungicidal composition according to claim 1 substantially as hereinbefore described with reference to Example 2.

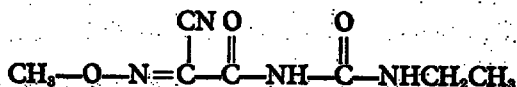
15. A method for the inhibition of fungus diseases in plants comprising applying to the locus of such disease a fungicidally effective amount of a mixture of any of claims 1—4.

16. A method for the inhibition of fungus diseases in plants comprising applying to the locus of such disease a fungicidally effective amount of a mixture of claim 2.

17. A method for the inhibition of fungus diseases in plants comprising applying to the locus of such disease a fungicidally effective amount of a mixture of claim 3.

18. A method for the inhibition of fungus diseases in plants comprising applying to the locus of such disease a fungicidally effective amount of a mixture of claim 4.

19. A method according to any of claims 15—18 wherein the weight ratio of



to said other fungicide is in the range 2:1 to 1:100.

20. A method according to any of claims 15—19 wherein said mixture is applied in admixture with an agricultural chemical selected from the list herein.

21. A method according to claim 15 substantially as hereinbefore described with reference to Example 1 or 2.

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