

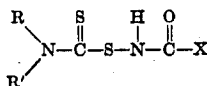
UNITED STATES PATENT OFFICE

FUNGICIDES

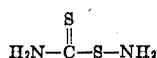
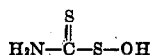
**No Drawing. Application August 31, 1945,
Serial No. 613,950**

19 Claims. (CL 167—38)

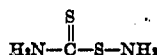
I have found that thiocarbamosulfenamides in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group, are effective fungicides. The structure of the compounds may be represented by the general formula



as the amide of the hypothetical thiocarbamo-
sulfenic acid



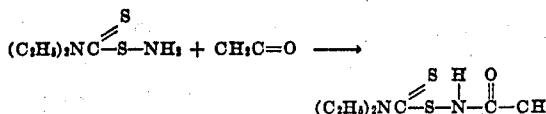
The compound



and the other to the sulfenamide group $-S-NH_2$. To differentiate these nitrogens, the thiocarbamo nitrogen is labeled "N" and the sulfenamide nitrogen is labeled "N'" in the nomenclature of the compounds. Thus, the thiocarbamo (N) nitrogen is a tertiary amino nitrogen in the compounds of the present invention, and the sulfenamide (N') nitrogen is a secondary nitrogen to which is attached an acyl group.

N,N-dimethyl N'-acetyl thiocarbamosulfenamide
N,N-diethyl N'-acetyl thiocarbamo sulfenamide
N,N-diallyl N'-acetyl thiocarbamo sulfenamide
N,N-dipropyl N'-acetyl thiocarbamo sulfenamide
N,N-diethyl N'-acetyl thiocarbamo sulfenamide
N,N-dibutyl N'-acetyl thiocarbamo sulfenamide
N,N-dibenzyl N'-acetyl thiocarbamo sulfenamide
N,N-dimethyl N'-propionyl thiocarbamo sulfenamide
N,N-dimethyl N'-butyryl thiocarbamo sulfenamide
N,N-dimethyl N'-valeryl thiocarbamo sulfenamide
N,N-diphenyl N'-acetyl dithiocarbamo sulfenamide
N-methyl, N-phenyl N'-acetyl dithiocarbamo sulfenamide
N-oxydiethylene N-acetyl thiocarbamosulfenamide

The following illustrates in more detail the preparation of the chemicals; e. g. N,N-diethyl N'-acetyl thiocarbamosulfenamide according to the equation:



To a solution of 35 g. N,N-diethyl thiocarbamo sulfenamide (U. S. Patent No. 2,318,482) in 200 cc. dry ether, ketene (from 500 cc. acetone) is introduced over a 6 hour period. The temperature of reaction is held at 20° C. and additional ether is added to keep the volume constant. At the end of the reaction the ether is evaporated and the residual oil crystallizes on standing. Recrystallized from a benzene-ligroin mixture. Melting point 67° C. Yield 19.6 g. The ketene was prepared by the pyrolysis of acetone in accordance with the usual procedure. The ketene $\text{CH}_2=\text{C}=\text{O}$ may also be prepared by the action

of zinc on bromoacetyl bromide or on chloroacetyl chloride in known manner. This latter method is the one used in preparing the higher ketenes as by the action of zinc on the appropriate α halo-

acetyl halide. Similarly, when N,N-dimethyl thiocarbamo sulfenamide is reacted with the ketene in the above procedure, there is obtained N,N-dimethyl N'-acetyl thiocarbamo sulfenamide, M. P. 135° C.; using morpholyl thiocarbamo sulfenamide for reaction with the same ketene in the above procedures results in N-oxydiethylene N'-acetyl thiocarbamo sulfenamide, M. P. 163-164° C.; using N,N-diphenyl thiocarbamo sulfenamide (M. P. 149° C.), there is obtained N,N-diphenyl N'-acetyl thiocarbamo sulfenamide, M. P. 167° C.; and from N-methyl N-phenyl thiocarbamo sulfenamide (M. P. 86-87° C.), N-methyl N-phenyl N'-acetyl thiocarbamo sulfenamide M. P. 127-128° C. is prepared.

The compounds of the present invention may be used as seed protectants and to protect plants, which term includes plant parts, and soil from microorganisms harmful to seeds and plants. They may also be applied to prevent or retard fungus growth and the formation of, for example, mildew on organic material such as cellulosic material, rope, wood, fur, hair, feathers, cotton, wool, and leather. They may be applied as a dust, undiluted or mixed with a powdered solid carrier, such as clay or talc, or as a liquid or spray in a liquid carrier, as in solution in a suitable solvent, or suspended in a suitable non-solvent, for example, water. Preferably when applied in aqueous suspension, the composition contains a dispersing agent for the chemicals. In seed treatment, the compounds of the present invention are preferably applied to the seeds as by tumbling with the straight chemical, or with the chemical admixed with a powdered solid carrier. In foliage treatment, the compounds of the present invention are preferably applied to the plant parts as by spraying with an aqueous suspension of the chemical containing a dispersing agent. Similar aqueous suspensions are preferred for the mildewproofing of textiles, such as cotton fabrics. The chemicals may be applied as to foliage by the aerosol method. Solutions for the aerosol treatment may be prepared by dissolving the chemical directly in the highly volatile liquid carrier or first dissolving the chemical in a less volatile solvent and then admixing such solution with the highly volatile liquid aerosol carrier. The compounds may be used admixed with carriers that are active of themselves, for example, other fungicides, or bactericides, insecticides, insectifuges, fertilizers, hormones, buffering or softening agents.

The following illustrates the invention:

Barley seeds, known to be infected with the destructive root rotting fungus *Helminthosporium sativum*, were tumbled with 1% by weight of the chemical of the invention under evaluation. Twenty-five of the seeds thus treated with one of the chemicals, and twenty-five of the infected seeds not treated with any chemical, were placed on pads of filter paper in separate petri dishes which contained 2 cc. of a 2% aqueous dextrose solution, and allowed to stand for six days at room temperature. This was repeated for various chemicals of the invention as shown in the table below. After the six days standing at room temperature, observations were made. Infection of the seeds that were not successfully disinfected, could readily be detected by the presence

of dark colored *Helminthosporium* sporulating on the surface of the seeds and in a narrow zone on the filter paper around the seeds. The seeds under test were scored as to percent control. In every run where the seeds were not treated with a chemical there was found one hundred percent infection (0% control). The control of the infection of seeds treated with chemicals of the invention are shown in the table below:

Chemical:	Per cent control
N,N-diethyl N'-acetyl thiocarbamo sulfenamide -----	100
N,N-diphenyl N'-acetyl thiocarbamo sulfenamide -----	100
N-methyl N-phenyl N'-acetyl thiocarbamo sulfenamide -----	76
N,N-dimethyl N'-acetyl thiocarbamo sulfenamide -----	100

Having thus described my invention, what I claim and desire to protect by Letters Patent is:

1. A fungicidal composition comprising as an active ingredient a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group, and a carrier therefor selected from the group consisting of powdered solid carriers, and water containing a dispersing agent.

2. A fungicidal composition comprising an aqueous suspension of a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

3. A fungicidal composition comprising an aqueous suspension of a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group, said aqueous suspension containing a dispersing agent.

4. A fungicidal composition comprising an aqueous suspension of N,N-dimethyl N'-acetyl thiocarbamo-sulfenamide.

5. A fungicidal composition comprising an aqueous suspension of N,N-dimethyl N'-acetyl thiocarbamo-sulfenamide containing a dispersing agent.

6. The method of protecting organic material subject to attack by microorganisms which comprises applying to said material a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

7. The method of controlling fungi on growing plants which comprises treating the foliage of the plants with a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

8. The method of controlling fungi on growing plants which comprises treating the foliage of the plants with N,N-dimethyl N'-acetyl thiocarbamosulfenamide.

9. The method of controlling fungi on growing plants which comprises spraying the foliage of the plants with a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a

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tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

10. The method of controlling fungi on growing plants which comprises spraying the foliage of the plants with N,N-dimethyl N'-acetyl thiocarbamosulfenamide.

11. The method of protecting seeds, plants and soil subject to attack or infestation by fungi which comprises treating said material with a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

12. The method of immunizing seed which comprises treating said seed with a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

13. The method of immunizing seed which comprises treating said seed with N,N-dimethyl N'-acetyl thiocarbamosulfenamide.

14. The method of controlling fungi on living organisms which comprises treating said organisms with a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

15. The method of controlling fungi on living organisms which comprises treating said organ-

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isms with N,N-dimethyl N'-acetyl thiocarbamosulfenamide.

16. The method of destroying fungus which comprises subjecting said fungus to the action of a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

17. The method of destroying fungus which comprises subjecting said fungus to the action of N,N-dimethyl N'-acetyl thiocarbamosulfenamide.

18. The method of controlling mildew on textiles which comprises treating said textiles with a thiocarbamosulfenamide in which the nitrogen of the thiocarbamo group is a tertiary-amino nitrogen and the nitrogen of the sulfenamide group has attached to it a hydrogen atom and an acyl group.

19. The method of controlling mildew on textiles which comprises treating said textiles with N,N-dimethyl N'-acetyl thiocarbamosulfenamide.

JOSEPH B. SKAPTASON.

REFERENCES CITED

The following references are of record in the file of this patent:

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