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3,102,840

METHOD OF CONTROLLING FUNGI WITH ESTERS OF O-PHENYL PHENOL

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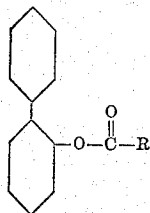
6 Claims. (Cl. 167—30)

The present invention relates to fungicidal compositions and to methods of using the same; and more particularly to organic fungicidal compositions which can be safely applied to materials normally susceptible to attack by fungus organisms. More specifically, the present invention is concerned with the application of organic fungicidal compositions to agricultural plant life, notably vegetables and fruits, to prevent or inhibit the growth of fungi therein.

Many fungicides, fungistats and fungitoxic agents are presently known and are used in tremendous quantities in industry to mitigate, inhibit or destroy fungi. In spite of the many types of fungicides known, there is a continuing search for additional fungicides which may prove of greater facility or safety in their application, of greater toxicity or desired specificity in their action, of greater economy or efficiency in their cost, and so forth.

It is therefore a principal purpose of the present invention to provide fungicidal, fungistatic or fungitoxic compositions which can be safely and easily applied to materials susceptible to fungus attack to provide protection against a diversity of fungus organisms under a diversity of conditions of use at a low enough cost to render their application economically feasible.

Such purposes may be realized by means of compositions having the following structural formula



in which R is a lower alkyl radical containing from 1 to 4 carbon atoms, such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl, and isobutyl. Such compounds are generically known as the lower alkyl esters of o-phenyl phenol and will be referred to as such in the following description of the invention.

These compounds, in their pure state, may be too effective, or too potent, or too costly in some applications, to warrant their use in such concentrated form. They are therefore used in a diluted, emulsified or dispersed form in an adjuvant fluid carrier, the most desirable being an aqueous media. The dilution of the fungicidal compounds of the present invention in such an adjuvant fluid carrier will depend on many factors, the predominant one being the intended use of the fungicide. A concentration of as low as about 5% by weight of fungicidal agent in the fungicidal composition has been found satisfactory in some uses, whereas up to about 65% or more by weight is required for other uses. Within the more commercial aspects of the invention, however, a concentration of from about 15% to about 45% by weight of the fungicide is preferred.

Strictly speaking, "fungicides" are referred to in industry by that term only if they are effective at nominal dosages of 1000 parts per million (0.001) or less, whereas the term "fungitoxic" is applied to those chemical agents

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which are not as effective. The term "fungistat" is applied to chemicals which inhibit spore germination or mycelial growth without destroying the fungous body. In common usage, all of these chemical agents, however, are loosely referred to as "fungicides" and such term will be similarly loosely used herein.

Also, the term "adjuvant," or "adjuvant carrier," as used herein, is intended in its broadest sense, namely, as an auxiliary or assistant ingredient, or any material which aids or modifies the action of the essential fungicidal agent.

Other materials may also be included in the fungicidal composition to modify or alter the general action or effect thereof. For example, surface active agents, emulsifiers, wetting, dispersing and suspending agents are desirably also incorporated in the aqueous fungicidal composition. The particular surfactant selected is a matter of choice and its selection may be made from a large group of such agents, such as the alkylaryl polyether alcohols such as "Triton X-45" and "Triton X-100" which are non-ionic; the fatty acid esters of polyhydric alcohols such as the "Spans" which are nonionic; the ethylene oxide addition products of such polyhydric alcohol esters such as the "Tweens" which are nonionic; the alkylpoly (ethyleneoxy) ethanols such as the "Emulphogenes" which are nonionic; the alkyl phenoxy poly (ethyleneoxy) ethanols such as the "Igepals" which are nonionic; the "Igepons" notably the sodium N-alkyl-N-oleoyl taurates which are anionic; metal soaps which are anionic; quaternary ammonium salts such as the "Hyamines" which are cationic; etc.

The amount of surfactant included in the aqueous fungicidal composition may be varied within relatively wide limits. In some cases, they may be omitted or be present in an amount equal to 1 or 2% by weight or less, and in other cases up to about 35% by weight or more is required. Normally, however, from about 5% to about 25% is found desirable commercially.

In addition to surfactants, various other materials may be included in the fungicidal composition for specially desired results. For example, solubility promoters, adherents or sticking agents such as vegetable oils, naturally occurring gums, glue, starch, and other adhesives may be added. Humectants may also be employed. Plant growth regulators similarly may be included. Other toxic agents such as insecticides, bactericides, larvacides, vermicides, miticides, etc., may also be included. Examples of such include organic sulfur fungicides, pyrethrum, malathion, chlordane, dichloro-diphenyl-trichloroethane; aldrin; dieldrin; etc. The amounts added to such additional materials will normally be small and normally but 1-2% by weight. Increased percentages up to 20% by weight may be used, when desired or required.

The percentages by weight set forth in the preceding paragraphs refer to the percentages by weight in commercial and industrial preparations to be sold to the public. In action use, such preparations may be diluted, as desired, by the addition of more aqueous media. The extent of the dilution will be determined primarily by the intended use. For certain uses, concentrations of active ingredient (the ester of o-phenyl phenol) of about 1 part in a million (0.000001) or less may be sufficient; for others, about 100 parts in a million (0.0001) may be required; for more drastic treatments, 10,000 parts in a million (0.01) or more may be necessary. Actual concentrations will be determined by actual uses and the invention is not to be construed as limited to any specific concentrations.

It is not necessary that the adjuvant carrier be an aqueous media. Other fluids, such as organic materials, may also be used where such fluids can be tolerated. For example, higher alcohols such as butanol and oleyl

alcohol, esters thereof, high boiling oils of vegetable origin, petroleum fractions, particularly naphtha and kerosene, aromatic compounds such as benzene and xylol, etc. are applicable.

For use as a powder or dust, the esters of o-phenyl phenol can be formulated, using any of a number of inert carriers or extending agents, either organic or inorganic in nature, which are suitable for the production of pulverulent materials. These include, for example, calcium carbonate, kaolin, kieselguhr, clay, lime, bentonite, pumice, fuller's earth, talc, magnesium carbonate, etc. These compositions may be used in the dry form, or by the addition of powdered wetting agents, the dried powder can be rendered wettable by water so as to obtain stable, aqueous dispersions suitable for use as sprays.

In preparing such concentrated wettable powders, it is preferred to use from about 0.1 to about 10 percent by weight of the wetting agent based upon the amount of active ingredients and from about 20 to about 90 percent of the inert carrier based on the total amount of the complete formulation. Such formulations provide the advantage of permitting easy storage and transportation of the fungicide and permitting further dilution by simple admixture with aqueous media at the time of application. Such finished formulations, depending on the application in mind, may include between about 1 to about 10,000 parts per million of active ingredient, with a preferred range of from about 2 to about 2000 parts per million.

The invention will be further illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe in particular detail some of the more specific features of the invention, they are given primarily for purposes of illustration and the invention in its broader aspects is not to be construed as limited thereto.

Example I

1360 grams (8 moles) of o-phenyl phenol (molecular weight 170) and 1040 grams (8 moles) of propionic anhydride (molecular weight 130) are weighed into a three-necked three-liter flask equipped with a stirrer, a thermometer, and a reflux condenser with adapters for distilling. The reaction mixture is heated with stirring for about one hour at a temperature ranging between 85° C. and 90° C. The pressure is then reduced to about 12-16 mm. and the temperature is raised to distill off the propionic acid and subsequently the desired reaction product identified as o-diphenyl propionate.

A fungicidal composition is then prepared as follows.

Materials:	Parts
o-Diphenyl propionate.....	25.0
Sulfated Emulphogene BC-420.....	10.0
Triton X-100.....	6.0
Triton X-45.....	3.0
Dow Anti-Foam B.....	0.5
Hyamine 2389.....	1.0
Water	54.5

All the materials except the o-diphenyl propionate and Hyamine 2389 are introduced into a mixing kettle at room temperature and stirred. The o-diphenyl propionate is then added slowly with stirring at room temperature. The Hyamine 2389 is then added. A stable emulsion results.

The fungicidal composition is tested in spore germination tests as follows: spores from a 1-week old culture of two fungi (1) *Alternaria oleracea* and (2) *Fusicoccum amygdali* are mixed (100 per field) with various dilutions of the composition being tested and placed in drops on glass slides. The glass slides are placed in moist chambers and incubated for 24 hours at a temperature of 72° F. Germination counts are as follows: the lowest concentration of the fungicidal composition inhibiting germination of *Alternaria oleracea* is 0.001; the lowest con-

centration inhibiting germination of *Fusicoccum amygdali* is 0.000001. Both of these results are satisfactory and establish the value of o-diphenyl propionate as a fungicide.

Example II

Additional samples of the o-diphenyl propionate fungicide prepared in Example I are diluted to concentration of 1.5 and 3 quarts per one hundred gallons of water and then sprayed on tomato plants in greenhouses. After the spray deposit has dried, spores of the fungus *Helminthosporium solani* producing the gray mold disease are sprayed on the tomato plants. This test is conducted under low light intensity and high humidity, which conditions are conducive to the development of soft, succulent low carbohydrate-containing tomato plants which are more susceptible to injury than are normal plants. In addition, the high humidity and wet surfaces increase the opportunities for solubilization of the fungicide thereby increasing its chances of being phytotoxic. In these tests, the o-diphenyl propionate fungicide prevents any injury to the tomato plants sprayed at either concentration. The amount of disease developed is insufficient to make disease readings of any value.

Example III

Beginning with the first scab spray (green leaves just showing) and continuing through four post bloom sprays (8 applications in all), the o-diphenyl propionate fungicide prepared in Example I is applied at concentrations of 1.5 and 3 quarts per 100 gallons of water to six randomized Rome apples per treatment. These applications are applied every seven to ten days through the test period. The conditions are dry with low humidity. Very little scab develops on the Rome apples.

Example IV

The procedures of Example I are followed substantially as set forth therein except that 816 grams (8 moles) of acetic anhydride (molecular weight 102) is used to replace the propionic anhydride. The resulting product is o-diphenyl acetate and similar evaluations establish it as possessing fungicidal properties.

Example V

The procedures of Example I are followed substantially as set forth therein except that 1264 grams (8 moles) of butyric anhydride (molecular weight 158) is used to replace the propionic anhydride. The resulting product is o-diphenyl butyrate and similar evaluations establish it as possessing fungicidal properties.

Although the present invention has been described with particular reference to the application of organic fungicidal compositions containing esters of o-phenyl phenol to agricultural plants, notably vegetables and fruits, it is to be appreciated that other agricultural applications such as to trees, shrubs, bushes, herbs, grains, etc. are also included. Other more general uses are also applicable. Examples of such other uses include the protection of cellulosic materials, wood, cotton cloth and other textiles, furs, leather, and other fibrous materials, from mildew, discoloration, mold or other rot organisms.

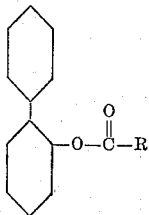
Although several specific examples of the inventive concept have been described, the same should not be construed as limited thereby nor to the specific substances mentioned therein but to include various other compounds of equivalent constitution as set forth in the claims appended hereto. It is understood that any suitable changes, modifications and variations may be made without departing from the spirit and scope of the invention.

What is claimed is:

1. The method for the treatment of plants which com-

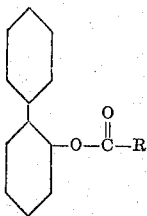
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prises treating said plants with a fluid suspension of a compound having the formula



in which R is a lower alkyl radical containing from 1 to 4 carbon atoms.

2. The method of preventing the growth of fungi which comprises exposing the fungi to a fungicidal quantity of a compound having the formula



in which R is a lower alkyl radical containing from 1 to 4 carbon atoms.

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3. The method of inhibiting fungus growth which comprises exposing the fungi to a fungicidal quantity of a lower alkyl ester of o-phenyl phenol.

4. The method of inhibiting fungus growth which comprises exposing the fungi to a fungicidal quantity of o-diphenyl acetate.

5. The method of inhibiting fungus growth which comprises exposing the fungi to a fungicidal quantity of o-diphenyl propionate.

6. The method of inhibiting fungus growth which comprises exposing the fungi to a fungicidal quantity of o-diphenyl butyrate.

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