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DIVISION DE NUEVAS CREACIONES

SUPERINTENDENCIA DE INDUSTRIA Y

Santafé de Bogotá, D C

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Solicitud de Patente

Debidamente traducida, adjunto acompaño la copia oficial de la solicitud de patente básica estadounidense No 09/391 292, la cual le solicito agregar a este expediente para los efectos legales respectivos

De Ustedes atentamente,

GERMAN CASTILLO GRAU

T.P. No 2978 del C S J

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NÚMERO DE SOLICITUD 09/391 292

FECHA DE RADICACIÓN 07 de septiembre de 1999

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No. 00046522-2

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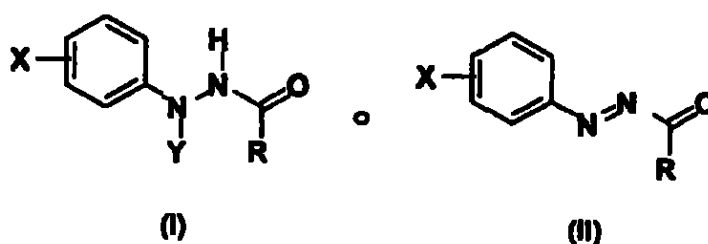
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METODO PARA CONTROLAR HONGOS UTILIZANDO DERIVADOS DE FENILHIDRAZINA

REIVINDICACIONES

1 Un metodo para el control de hongos que consiste en hacer contactar los hongos con una cantidad fungicidamente efectiva de un compuesto derivado de fenilhidrazina de la fórmula



en donde

X es a) fenil, fenil (alcoxi C₁-C₄), fenoxi, o bencil, o b) un sustituyente del grupo a) y uno o más sustituyentes seleccionados de halógeno, alquil C₁-C₄, y alquiltio C₁-C₄,

Y es H, alcoxi C₁-C₄, haloalcoxi C₁-C₄, o (alcoxi C₁-C₄) carbonil, y

R es H, alquil C₁-C₆, haloalquil C₁-C₆, alcoxi C₁-C₆, haloalcoxi C₁-C₆, o fenil (alcoxi C₁-C₄)

2 El método según la reivindicación 1, en donde

X es a) fenil, fenil (alcoxi C₁-C₄), fenoxi, o bencil, o b) un sustituyente del grupo a) y uno o mas sustituyentes seleccionados de halógeno, alquil C₁-C₄, y alquiltio C₁-C₄,

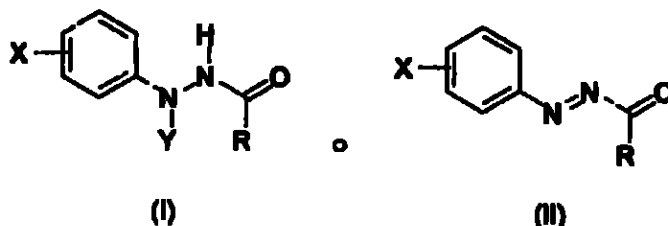
Y es H, alcanoil C₁-C₂, haloalcanoil C₁-C₂, o (alcoxi C₁-C₂) carbonil, y

R es H, alquil C₁-C₄, haloalquil C₁-C₄, alcoxi C₁-C₄, haloalcoxi C₁-C₄, o fenil (alcoxi C₁-C₄)

3 El método según la reivindicación 2, en donde X es fenilmetoxi, fenoxi, o fenil y halógeno o alquiltio C₁-C₂, Y es hidrógeno o haloalcanoil C₁-C₂, y R es alcoxi C₁-C₄ o haloalcoxi C₁-C₄

4 El método según la reivindicación 3, en donde X es fenoxi, Y es hidrógeno, y R es alcoxi C₁-C₄

5 Un metodo para el control de hongos en una planta o semilla que consiste en aplicar a la planta o a la semilla, o a un medio de crecimiento o agua donde crezca o donde vaya a crecer la planta o la semilla, en una cantidad fungicidamente efectiva de un compuesto derivado de fenilhidrazina de la fórmula



en donde

X es a) fenil, fenil (alcoxi C₁-C₄), fenoxi, o bencil, o b) un sustituyente del grupo a) y uno o mas sustituyentes seleccionados de halógeno, alquil C₁-C₄, y alquiltio C₁-C₄,

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Y es H, alcanoil C₁-C₄, haloalcanoil C₁-C₄, o (alcoxi C₁-C₄) carbonil,
y

R es H, alquil C₁-C₆, haloalquil C₁-C₆, alcoxi C₁-C₆, haloalcoxi C₁-C₆,
o fenil (alcoxi C₁-C₄)

6 El método según la reivindicación 5, en donde

X es a) fenil, fenil (alcoxi C₁-C₄), fenoxi, o bencil, o b) un sustituyente
del grupo a) y uno o mas sustituyentes seleccionados de halógeno, alquil
C₁-C₄, y alquiltio C₁-C₄,

Y es H, alcanoil C₁-C₂, haloalcanoil C₁-C₂, o (alcoxi C₁-C₂) carbonil, y

R es H, alquil C₁-C₄, haloalquil C₁-C₄, alcoxi C₁-C₄, haloalcoxi C₁-C₄,
o fenil (alcoxi C₁-C₄)

7 El método según la reivindicación 6, en donde X es fenilmetoxi,
fenoxi o fenil y halogeno o alquiltio C₁-C₂, Y es hidrógeno o haloalcanoil C₁-
C₂, y R es alcoxi C₁-C₄ o haloalcoxi C₁-C₄

8 El metodo segun la reivindicación 7, en donde X es fenoxi, Y es
hidrógeno, y R es alcoxi C₁-C₄

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Issued pursuant to CHXIV Stat. of
Sept. 15, 1789, 1 Stat. 68-69- 22
USC 2657- 22 USC 2651a, 5 USC
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APPLICATION NUMBER 09/391,292✓

FILING DATE September 07, 1999



**By Authority of the
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Docket No 6381
Inventors Dekeyser et al
Express Mail Label No. EE021528760US

Handwritten: A-48, 45

Assistant Commissioner for Patents
Box Patent Application
Washington, D C. 20231



UTILITY PATENT APPLICATION TRANSMITTAL UNDER 37 CFR 1.53(b)

Sir

Enclosed herewith for filing are

1 The patent application of

Inventors Mark Achuel Dekeyser, Kenneth Wesley Seebold, Jr., and Gaik-Lean Chee

Title METHOD FOR CONTROLLING FUNGI USING PHENYLHYDRAZINE DERIVATIVES

Total pages - 28

2 Application

- a ☒ New Application
b ☐ Continuation ☐ Divisional ☐ Continuation-in-part
of U S Application Serial No , filed on

3 ☐ sheets of drawings

4 Oath or Declaration (Total pages - 2)

- a. ☒ Newly executed (original or copy)
b ☐ Copy from prior application (37 CFR 1.63(d))
(for continuation/divisional application)

5 ☐ Incorporation By Reference

The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4 above, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein

6 ☒ An assignment of the invention to Uniroyal Chemical Company, Inc. and Uniroyal Chemical Co./Cie, and cover sheet.

7 ☒ Power of Attorney

8 ☐ Information Disclosure Statement/PTO 1449

9 ☐ Preliminary Amendment

662060-26216E60

10 (X) Return Receipt Postcard

11 0 Other

12 The fee has been calculated as shown below

	Claims Filed	Extra Claims	Rate	Fee
Basic Fee				\$760
Total Claims	8-20	0	X \$18	\$0
Independent Claims	2-3	0	X \$78	\$0
[] Multiple dependent claims presented			+ \$260	\$0
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Respectfully submitted,



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METHOD FOR CONTROLLING FUNGI USING
PHENYLHYDRAZINE DERIVATIVES

5 Field of the Invention

This invention relates to a method for controlling fungi using certain phenylhydrazine derivatives. More particularly, this invention relates to a method for controlling fungi by contacting the fungi with a fungicidally effective amount of a phenylhydrazine derivative compound, or by applying the phenylhydrazine derivative compound to plant foliage or plant seed susceptible to attack by said fungi, or to a growth medium for the plant to be protected.

10

15 Background of the Invention

U S Patent No 5,367,093 describes phenylhydrazine derivative compounds useful as insecticides, acaricides and nematocides. Japanese patent JP02300157 1990 (CA 115 226148) describes benzyl carbazates useful as agrochemical microbiocides. Japanese patent JP02295962 1990 (CA 114 138036) describes the preparation of phenyl carbazates useful as agrochemical fungicides. Japanese patent JP60161959 1985 (CA 104 33894) describes hydrazine carboxylates useful as fungicides. German patent DE2223936 1973 (CA 80 70557) describes fungicidal arylhydrazine derivatives.

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It is an object of this invention to provide a novel method for controlling fungi using phenylhydrazine derivative compounds and compositions.

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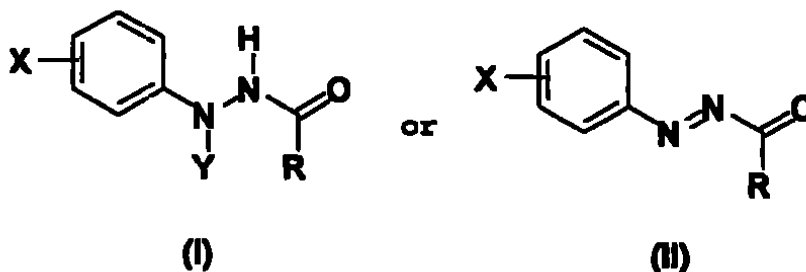
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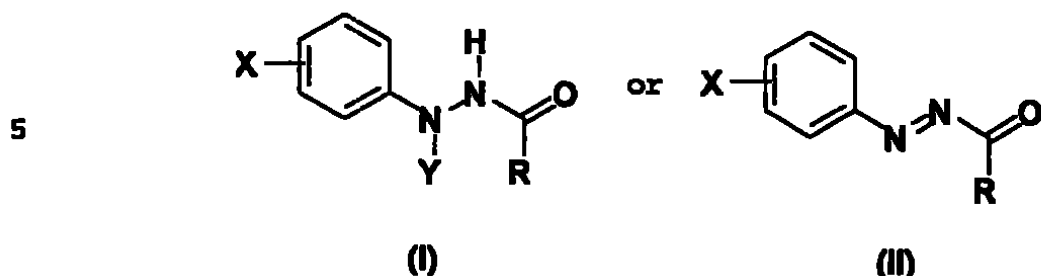
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Summary of the Invention

This invention relates to a method for controlling fungi, particularly phytopathogenic fungi, comprising contacting the fungi with a fungicidally effective amount of a phenylhydrazine derivative compound of the formula



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10 wherein

X is a) phenyl, phenyl(C₁-C₄ alkoxy), phenoxy, or benzyl, or b) one substituent from group a) and one or more substituents selected from halogen, C₁-C₄ alkyl, and C₁-C₄ alkylthio,

Y is H, C₁-C₄ alkanoyl, C₁-C₄ haloalkanoyl, or (C₁-C₄ alkoxy)carbonyl, and

R is H, C₁-C₆ alkyl, C₁-C₆ haloalkyl, C₁-C₆ alkoxy, C₁-C₆ haloalkoxy, or phenyl(C₁-C₄ alkoxy)

Detailed Description of the Invention

For the purposes of this invention, the term "controlling fungi" means inhibiting both future infestation and continued growth of existing infestations

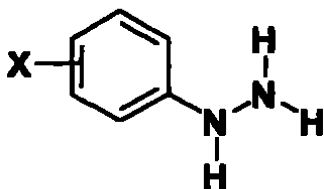
In the compounds useful in the method of this invention, X is preferably, a) phenyl, phenyl(C₁-C₂ alkoxy), or phenoxy, or b) one substituent from group a) and one or more substituents selected from halogen, C₁-C₂ alkyl, and C₁-C₂ alkylthio,

Y is preferably H, C₁-C₂ alkanoyl, C₁-C₂ haloalkanoyl, or (C₁-C₂ alkoxy)carbonyl, and

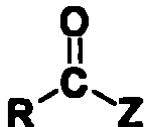
R is preferably H, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, or phenyl(C₁-C₂ alkoxy)

X is more preferably phenylmethoxy, phenoxy, or phenyl and halogen or C₁-C₄ alkylthio, most preferably, phenoxy, Y is more preferably hydrogen or C₁-C₂ haloalkanoyl, most preferably, hydrogen, and R is more preferably C₁-C₄ alkoxy or C₁-C₄ haloalkoxy, most preferably, C₁-C₄ alkoxy

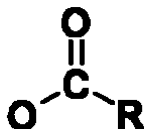
The compounds useful in the method of this invention having the structure of formula I can be prepared by reacting a substituted phenylhydrazine of the formula



with an acylating reagent of the formula



wherein Z is halo or



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and an equivalent of an HCl acceptor such as pyridine in a solvent such as toluene. The product of this reaction can be further acylated, or converted by oxidation with an oxidizing agent such as Pd/air to form compounds of the structure of formula II

Compositions useful in the method of this invention comprise (a) a fungicidally effective compound having a structure of formula (I) or (II) above, and (b) a suitable carrier. Such suitable carriers may be solid or liquid in nature

Suitable liquid carriers may be comprised of water, alcohols, ketones, phenols, toluene and xylenes. In such formulations, additives conventionally employed in the art may be utilized such as, for example, one or more surface active agents and/or inert diluents, to facilitate handling an application of the resulting pesticide composition

The compositions useful in the method of this invention can alternatively comprise solid carriers taking the form of dusts, granules, wettable powders, pastes, aerosols, emulsions, emulsifiable concentrates, and water-soluble solids

For example, the compounds useful in the method of this invention can be applied as dusts when admixed with or absorbed onto powdered solid carriers, such as mineral silicates, e.g., mica, talc, pyrophyllite and clays, together with a surface-active dispersing agent so that a wettable powder is obtained which then is applicable directly to the loci to be treated. Alternatively, the powdered solid carrier containing the compound admixed therewith may be dispersed in water to form a suspension for application in such form

Granular formulations of the compounds, suitable for application by broadcasting, side dressing, soil

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incorporation or seed treatment, are suitably prepared using a granular or pelletized form of carrier such as granular clays, vermiculite, charcoal or corn cobs

Alternatively, the compounds useful in the method of this invention can be applied in liquids or sprays when utilized in a liquid carrier, such as in a solution comprising a compatible solvent such as acetone, benzene, toluene or kerosene, or as dispersed in a suitable non-solvent medium, for example, water

Another method of application to the loci to be treated is aerosol treatment, for which the compound may be dissolved in an aerosol carrier which is a liquid under pressure but which is a gas at ordinary temperature (e g , 20°C) and atmospheric pressure. Aerosol formulations may also be prepared by first dissolving the compound in a less volatile solvent and then admixing the resulting solution with a highly volatile liquid aerosol carrier

For treatment of plants (such term including plant parts), the compounds useful in the method of this invention preferably are applied in aqueous emulsions containing a surface-active dispersing agent which may be non-ionic, cationic or anionic. Suitable surface-active agents include those known in the art, such as those disclosed in U S Patent 2,547,724 (columns 3 and 4). The compounds of the invention may be mixed with such surface-active dispersing agents, with or without an organic solvent, as concentrates for the subsequent addition of water to yield aqueous suspensions of the compounds at desired concentration levels

In addition, the compounds may be employed with carriers which are pesticidally active, such as insecticides, acaricides, fungicides or bactericides

It will be understood that the amount of the

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compound in a given formulation useful in the method of this invention will depend upon the specific fungus to be combatted, as well as upon the specific chemical composition and formulation of the compound being employed, the method of applying the compound/formulation and the locus of treatment so that the fungicidally effective amount of the compound may vary widely

Generally, however, concentrations of the compound as the active ingredient in fungicidally effective formulations in the method of this invention can range from about 0.1 to about 95 percent by weight. Spray dilutions may be as low as a few parts per million, while at the opposite extreme, full strength concentrates of the compound may be usefully applied by ultra low volume techniques. Concentration per unit area, where plants constitute the loci of treatment, may range between about 0.01 and about 50 pounds per acre, with concentrations of between about 0.1 and about 10 pounds per acre preferably being employed for crops such as corn, tobacco, rice and the like.

To control fungi, sprays of the compounds can be applied to the fungi directly and/or to plants or plant seeds upon which they feed or nest. The fungicidally active formulations useful in the method of this can also be applied to the soil, water, or other growth medium in which the pests are present.

The specific methods of application, as well as the selection and concentration of the compounds useful in the method of this invention, will, of course, vary depending upon such circumstances as geographic area, climate, topography, plant tolerance, etc. For specific circumstances, one skilled in the art may readily determine the proper compound, concentration and method of application by routine experimentation.

Examples of phytopathogenic fungi which can be controlled by the method of this invention include, e g , the following

- 5 *Erysiphe graminis* f sp *hordei*
 Erysiphe cichoracearum
 Erysiphe polygoni
 Pyricularia grisea
 Helminthosporium sativum
10 *Uromyces appendiculatus*
 Botrytis cinerea
 Colletotrichum gossypii
 Cercosporidium personatum
 Fusarium nivale
15 *Phytophthora infestans*
 Pythium ultimum
 Rhizoctonia solani
 Sclerotinia minor
 Septoria nodorum

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55 ~~58~~**EXAMPLES**

The following examples are provided to further illustrate the invention

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Example 1

Preparation of 2,2,2-trichloroethyl 2-(4-phenylmethoxy)-phenylhydrazine carboxylate (Compound 1)

10 To 2 72 g of 4-(phenylmethoxy)phenylhydrazine, 100 ml of ethyl acetate and 2 5 ml of pyridine were added and the resulting solution was stirred at room temperature for 60 minutes. Then, 2 3 ml of 2,2,2-trichloroethyl chloroformate was added dropwise to the solution and then
15 stirred for 1 hour at room temperature. The solution was then washed twice, each time with 100 ml of water. After each wash, the aqueous fraction was removed from the organic (ethyl acetate) fraction. The resulting ethyl acetate fraction was then dried over anhydrous sodium
20 sulfate, evaporated under reduced pressure, and then purified by column chromatography on silica gel, to produce 0 5 g of 2,2,2-trichloroethyl 2-(4-phenylmethoxy)phenylhydrazine carboxylate as an oil.

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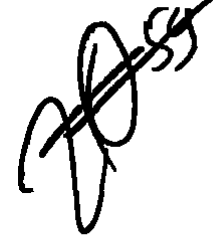
Example 2

Preparation of 2,2,2-trichloroethyl 2-(4-phenylmethoxy)-2-(trifluoroacetyl)phenylhydrazine carboxylate (Compound 2)

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To 0 5 g of the product of Example 1 was added 25 ml of dichloromethane and 0 5 ml of trifluoroacetic anhydride. The resultant reaction mixture was then
35 stirred at room temperature for 4 hours, concentrated under reduced pressure, and the concentrate isolated, to

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produce 0.6 g of 2,2,2-trichloroethyl 2-(4-phenylmethoxy)-2-(trifluoro-acetyl)phenylhydrazine carboxylate as a solid

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Example 3

Preparation of 1-methylpropyl 2-(3-phenoxyphenyl)-hydrazine carboxylate (Compound 3)

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10 To 3.0 g of 3-phenoxyphenyl hydrazine, 100 ml of ethyl acetate and 2.5 ml of pyridine were added and the resultant solution was then stirred at room temperature for 30 minutes. Then, 2.5 ml of sec-butyl chloro-formate was added dropwise to the solution and stirred for 1 hour

15 at room temperature. The solution was then washed twice, each time with 100 ml of water. After each wash, the aqueous fraction was removed from the organic (ethyl acetate) fraction. The resulting ethyl acetate fraction was then dried over anhydrous sodium sulfate, evaporated

20 under reduced pressure, and then purified by column chromatography on silica gel, to produce 1.5 g of 1-methylpropyl 2-(3-phenoxyphenyl)hydrazine carboxylate as an oil.

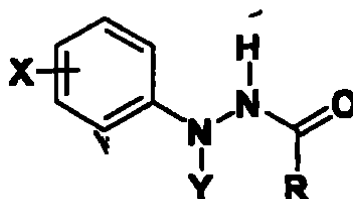
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The remaining compounds listed in Table 1A (i.e., Compounds 4-6) were prepared using the same procedures as shown in the foregoing examples 1-3 using the correspondingly different substituted phenylhydrazine

30 Each of the compounds is characterized by their NMR characteristics

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TABLE 1A



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10

Cmpd	X	Y	R	NMR DATA (CDCl ₃)
1	4-OCH ₂ C ₆ H ₅	H	OCH ₂ CCl ₃	s(2) 4 7, s(2) 4 9, s(1) 5 7, m(10) 6 8-7 4
2	4-OCH ₂ C ₆ H ₅	CF ₃ CO	OCH ₂ CCl ₃	s(2) 4 8, s(2) 4 9, m(9) 6 9-7 5
3	3-OC ₆ H ₅	H	OCH(CH ₃)C ₂ H ₅	t(3) 0 8, d(3) 1 2, m(2) 1 5, m(1) 4 8, s(1) 6 5, m(10) 6 9-7 4
4	2-Br, 5-C ₆ H ₅	H	OCH ₃	s(3) 3 8, s(1) 6 5, m(10) 6 9-7 5
5	2-SCH ₃ , 5-C ₆ H ₅	H	OCH ₃	s(3) 2 4, s(1) 6 5, m(10) 7 0-7 5
6	4-OC ₆ H ₅	H	OCH ₂ C ₆ H ₅	s(2) 5 1, s(1) 6 5, m(15) 6 8-7 4

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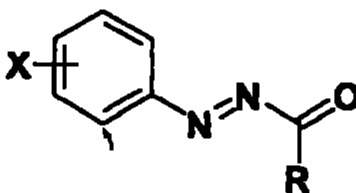
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Example 4Preparation of 1-methylpropyl(3-phenoxyphenyl)diazene carboxylate (Compound 7)

To 1.5 g of the product of Example 3 was added 100 ml of toluene and 0.4 g of 10% palladium on charcoal. The resultant mixture was stirred overnight at room temperature, filtered, and the toluene evaporated under reduced pressure, to produce 1.3 g of 1-methyl-propyl(3-phenoxyphenyl)diazene carboxylate as a red oil.

Table 1B



Compd	X	R	NMR DATA (CDCl ₃)
7 ✓	3-OC ₆ H ₅	OCH(CH ₃)C ₂ H ₅	t(3) 1.0; m(2) 1.5, m(1) 5.0, m(9) 7.0-7.5

59 Preparation of fungicidal compositions

The compounds listed below in Table 3 were each dissolved in acetone or another suitable solvent (0.3 grams of each compound in 10 ml of acetone or other suitable solvent). One to two drops of Tween 20®, a polyoxyethylene sorbitan ester used as an emulsifying agent, were added to water, followed by the acetone solution containing one of the compounds listed in Table 3. The amount of water added to the final solution varied according to the desired concentration, reported in parts per million (ppm).

Control of powdery mildew by foliar application

The barley cultivar 'Rodeo' was seeded into 4-inch-diameter pots containing a suitable medium for plant growth and allowed to grow for six days. Each treatment, or chemical, listed in Table 3 was replicated twice, and each pot contained eight plants. For each test, two pots of barley were left untreated to serve as controls.

Each of the compounds tested was formulated as described previously at a concentration of 1000 mg of compound per liter of water (1000 ppm), or 300 mg of compound per liter of water (300 ppm) in the case of Compound 2 and Compound 5. The resultant emulsion was applied to the foliage of the barley using an atomizer pressurized to 25-30 pounds per square inch. The treated plants, along with the untreated controls, were placed in a greenhouse and held at 21-25°C. One day following treatment, all plants were inoculated with conidia of *Erysiphe graminis* f. sp. *hordei* by brushing the leaves of mildew-infected barley plants over the leaves of the treated plants. One week after treatment, plants were rated for symptoms of powdery mildew using a 0-6 scale.

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where 0=no disease and 6=severe symptoms of mildew
Percent control was computed by comparing disease ratings
of treated plants to those from untreated plants The
results of these tests are provided in Table 4A under the
5 heading "Barley PM"

The compounds in Table 3 were tested for the control
of powdery mildew of bean, caused by *Erysiphe polygoni* by
preparing pots containing pinto bean (*Phaseolus vulgaris*)
in the same manner as described for barley Methods for
10 application of the chemical, inoculation with the
pathogen, and rating of disease were identical to those
described in the previous paragraph The results of
these tests are located in Table 4A under the heading
"Bean PM"

15 Control of powdery mildew by systemic root uptake

Compounds listed in Table 3 were prepared as
described previously and tested for efficacy against
powdery mildew of barley, caused by *Erysiphe graminis*
20 f sp hordei, and powdery mildew of cucumber, caused by
Erysiphe cichoracearum Each compound was evaluated for
prevention or control of powdery mildew when applied as a
soil drench, resulting in uptake of the compounds in
question by the roots of barley or cucumber and then
25 systemic distribution to the foliage

Pots of barley (cv "Robust") or cucumber (cv
"Marketmore 70") were grown in the same manner as barley
plants used for foliar applications Pots containing
barley had eight plants, while pots containing cucumber
30 held two plants Approximately one week after planting,
45 ml of an emulsion composition, formed as described
previously, was added to pots containing either barley or
cucumber Specifically, each 45ml of each compound was

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5 drenched into the soil of two pots containing barley and
two pots containing cucumber at a rate of 250 g of
compound per liter of water (250 ppm) Two compounds,
Compound 2 and Compound 5, were tested at a concentration
10 of 300 g of compound per liter of water (300 ppm) Two
pots each of barley and cucumber were left untreated to
serve as controls for the experiment Inoculation of the
plants was carried out as described previously, and
plants were rated for symptoms of powdery mildew one week
15 following treatment using a 0-6 scale where 0=no disease
and 6=severe symptoms of powdery mildew Percent control
was calculated by comparing ratings of treated plants to
those from untreated plants Results of these tests are
found in Table 4B under the headings "Barley PM" and
"Cucumber PM"

Control of Barley Blast by Foliar Treatment

20 Five barley plants (cv "Rodeo") were grown in 4-
inch-diameter pots, with two replicates for each
treatment An untreated check was also included and was
replicated twice Non-control pots were sprayed with
emulsion compositions prepared as described previously,
with each composition being tested at a concentration of
1000 ppm Compound 2 and Compound 5 were tested at a
25 concentration of 300 ppm The average plant age was 10
days Twenty-four hours after application of the
compositions, treated and untreated pots were inoculated
with the pathogen, *Pyricularia grisea*, at a concentration
30 of 40,000 to 50,000 conidia ml⁻¹ as a foliar spray Tween
20® was added (0.05% v/v) to aid in wetting of the
foliage, and plants were sprayed to runoff with the
conidial suspension

All inoculated pots were placed in an environmental
chamber set to maintain 26°C and >95% relative humidity

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Barley plants were incubated for 24 hours in the chamber, after which they were transferred to a greenhouse and observed for the development of symptoms of blast (6-7 days post-inoculation) Disease was evaluated using a 0-6 rating scale where 0=no blast lesions present and 6=severe symptoms Percent control of blast was calculated by comparing ratings of treated plants to those from untreated plants The results of these tests are located in Table 4A under the heading "Barley Blast"

Control of Barley Spot Blotch by Foliar Treatment

Two pots, each containing 10 barley plants (cv Robust), were planted Plants were treated with the previously described compositions that had been formulated in the same manner as for earlier examples Treated and untreated (control) pots were then inoculated with an aqueous inoculum suspension consisting of 20,000 conidia ml⁻¹ of *Helminthosporium sativum* and 2 drops of Tween 20® per 100 ml of solution were added to improve wetting The inoculation and incubation procedure was identical to that used in barley blast tests

Inoculated plants were then placed in a greenhouse and observed for development of symptoms, normally 6-7 days post-inoculation Disease was evaluated using a 0-6 rating scale where 0=no blotch lesions present and 6=severe symptoms Percent control was determined by comparing ratings from treated plants to ratings from untreated control plants Results for these are located in Table 4A "Barley Blotch"

Eradication of Bean Rust by Foliar Application

Two pinto bean plants (*Phaseolus vulgaris*) were planted in 4-inch-diameter pots and replicated twice Ten days after planting, when primary leaves had emerged,

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plants to be treated or left untreated as controls were inoculated with an aqueous suspension of uredospores of the bean rust pathogen, *Uromyces appendiculatus*. The inoculum was adjusted to a concentration of 20,000 uredospores ml⁻¹, and 2 drops of Tween 20® per 100 ml of solution were added to improve wetting. Inoculated plants were then placed in an environmental chamber set to maintain 26° C and >95% relative humidity. Twenty-four hours after inoculation, plants were removed and treated with the previously described fungicidal compositions at identical rates. Two pots were left untreated to serve as controls. Immediately following treatment, plants were placed in a greenhouse and observed for symptom development (5-7 days after inoculation). Disease was assessed on a 0-6 rating scale, where 0=no symptoms and 6=severe symptoms of bean rust. Percent control was calculated by comparing disease ratings from treated plants to ratings from untreated plants. The results of these experiments are detailed in Table 4A under the heading "Bean Rust".

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Table 4A
Percent control of phytopathogenic fungi in vivo
Foliar Application

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Cmpd	Barley PM	Barley Blast	Bean PM	Barley Blotch	Bean Rust
	1000 ppm	1000 ppm	1000 ppm	1000 ppm	1000 ppm
1	0	0	0	0	0
3	90	70	90	100	0
4	0	65	100	100	85
6	0	0	0	0	0
7	0	35	100	70	0
	300 ppm	300 ppm	300 ppm	300 ppm	300 ppm
2	0	0	0	0	0
5	0	0	0	0	0

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Table 4B
Percent control of phytopathogenic fungi in vivo
Drench Application

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Compd	Barley PM	Cucumber PM
	250 ppm	250 ppm
1	0	0
3	0	0
4	0	0
6	0	0
7	20	0
	300 ppm	300 ppm
2	0	0
5	0	0

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66 Control of Nine Species of Fungi in vitro

Each of the compounds listed in Table 3, with the exception of Compound 5, was solubilized in acetone to arrive at a final concentration of 500 ppm. Filter paper disks with a diameter of 11 mm were immersed in each of the test solutions and then allowed to air-dry so that the solvent evaporated from the disk. Two disks per treatment were prepared, and an equal number of disks were left untreated to serve as controls.

Treated and untreated disks were then placed on 110 x 15 mm petri plates containing solidified potato-dextrose agar (PDA). A sufficient number of treated and untreated disks were prepared to allow testing of all fungicidal compositions for the control of *Botrytis cinerea* (*B. cinerea*), *Colletotrichum gossypii* (*C. gossypii*), *Cercosporidium personatum* (*C. personatum*), *Fusarium nivale* (*F. nivale*), *Phytophthora infestans* (*P. infestans*), *Pythium ultimum* (*P. ultimum*), *Rhizoctonia solani* (*R. solani*), *Sclerotinia minor* (*S. minor*), and *Septoria nodurum* (*S. nodurum*). Treated and untreated disks were inoculated by placing a 6 mm plug, cut from an actively growing area of a culture of each of the fungi listed, in the center of the disk. The plug was oriented on the disk so as to allow the mycelial mat of the plug to contact the treated or untreated disk. In the case of *C. personatum*, two drops of a conidial/mycelial suspension, adjusted to a concentration of 20,000 propagules per ml⁻¹, were placed on the surface of untreated and treated disks.

The plates containing the inoculated disks were then placed in a gravity-type incubator set at 25° C and incubated for 5-7 days. Growth inhibition was evaluated

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by measuring the radius of the fungal colonies emanating from the original plug of inoculum on treated disks and comparing these measurements with those taken from untreated disks. The results of in vitro testing are located in Tables 5A and 5B.

In the case of Compound 5, a different method was used to assay fungicidal activity against the previously listed fungal species. A stock solution of each of the fungicidal compositions previously described was prepared by dissolving 0.01 g of the compound into 0.75 ml of acetone to achieve a final concentration of 15,000 ppm. A 1 μ l drop of each of the test compounds was then added to individual wells in a 96-well microtiter plate containing 50 μ l of potato-dextrose broth. Four wells in each plate were left untreated to serve as controls.

A suspension containing 10,000 cell fragments or conidia ml^{-1} (depending upon the fungus) was prepared by scraping petri plates containing active cultures of each of the test fungi with a rubber policeman, and homogenizing the resultant suspension with a glass tissue grinder. The final concentration was measured using a hemacytometer, and 50 μ l of the fungal suspension was added to each of the wells in the previously treated microtiter plate. Separate plates were used for each fungus, and the final concentration of test chemical was 150 ppm. Prior to incubation, each plate was placed on an eight-channel photometric microplate reader, set to measure absorbance at 492 nm, and an initial reading was taken to establish a baseline for each cell in the microplate.

Microtiter plates were then incubated for 48 hours in an incubation chamber set to maintain 26°C to allow for optimal growth of the test fungi. Following incubation, the microtiter plates containing the test

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5 fungi were removed and evaluated with the photometric
microplate reader described earlier. In principle, as
fungal growth increases, the optical density of the
solution in the individual wells of the microplate
increases and can be measured photometrically.
Therefore, readings taken following incubation of the
microplates containing test chemicals and fungi were
subtracted from the initial readings to measure the
amount of growth over the 48-hour period. Percent
10 inhibition of each fungus by the test chemicals was
calculated by comparing absorbance values from treated
wells to those that were untreated. The results of this
testing of Compound 5 can be found in Tables 5A and 5B.

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Table 5A

Percent control of phytopathogenic fungi in vitro

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Cmpd	<i>B</i> <i>cinerea</i>	<i>C</i> <i>gossypii</i>	<i>C</i> <i>personatum</i>	<i>F</i> <i>nivale</i>	<i>P</i> <i>infestans</i>
	500 ppm	500 ppm	500 ppm	500 ppm	500 ppm
1	10	80	0	0	85
2	91	100	100	10	0
3	85	100	0	84	100
4	100	100	100	100	80
6	85	100	0	100	60
7	100	100	100	100	100
	150 ppm	150 ppm	150 ppm	150 ppm	150 ppm
5	90	10	0	70	45

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Table 5B

Percent control of phytopathogenic fungi in vitro

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Cmpd	<i>P ultimum</i>	<i>R solani</i>	<i>S minor</i>	<i>S nodurum</i>
	500 ppm	500 ppm	500 ppm	500 ppm
1	100	5	0	25
2	47	0	5	-
3	100	78	100	90
4	100	70	100	75
6	45	0	100	0
7	70	75	100	100
	150 ppm	150 ppm	150 ppm	150 ppm
5	0	85	45	-

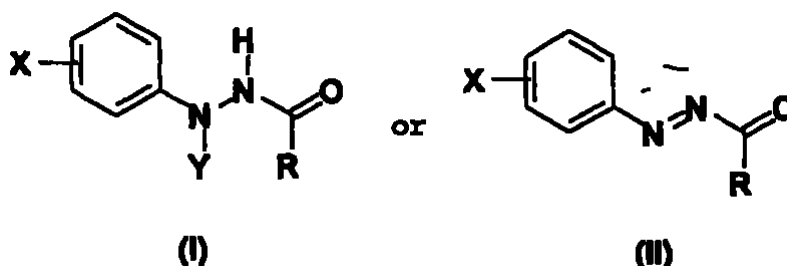
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WHAT IS CLAIMED IS

1 A method for controlling fungi comprising
contacting the fungi with a fungicidally effective amount
5 of a phenylhydrazine derivative compound of the formula



15 wherein

X is a) phenyl, phenyl(C₁-C₄ alkoxy), phenoxy, or
benzyl, or b) one substituent from group a) and one or
more substituents selected from halogen, C₁-C₄ alkyl, and
20 C₁-C₄ alkylthio,

Y is H, C₁-C₄ alkanoyl, C₁-C₄ haloalkanoyl, or (C₁-C₄
alkoxy)carbonyl, and

R is H, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy,
C₁-C₄ haloalkoxy, or phenyl(C₁-C₄ alkoxy)

25 2 The method as recited in claim 1 wherein

X is a) phenyl, phenyl(C₁-C₂)alkoxy, or phenoxy, or
b) one substituent from group a) and one or more
substituents selected from halogen, C₁-C₂ alkyl, and C₁-C₂
30 alkylthio,

Y is H, C₁-C₂ alkanoyl, C₁-C₂ haloalkanoyl, or (C₁-C₂
alkoxy)carbonyl, and

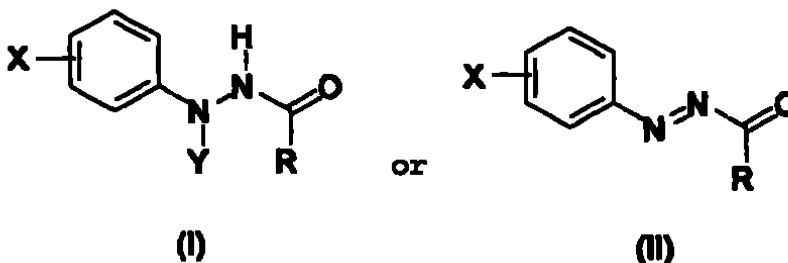
R is H, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy,
C₁-C₄ haloalkoxy, or phenyl(C₁-C₄ alkoxy)

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3 The method as recited in claim 2 wherein X is phenylmethoxy, phenoxy, or phenyl and halogen or C₁-C₂ alkylthio, Y is hydrogen or C₁-C₂ haloalkanoyl, and R is C₁-C₄ alkoxy or C₁-C₄ haloalkoxy

4 The method as recited in claim 3 wherein X is phenoxy, Y is hydrogen, and R is C₁-C₄ alkoxy

5 A method for controlling fungi on a plant or plant seed which comprises applying to the plant or the plant seed, or to a growth medium or water in which the plant or plant seed is growing or is to be grown in a fungicidally effective amount of a phenylhydrazine derivative compound of the formula



25 wherein

X is a) phenyl, phenyl(C₁-C₄ alkoxy), phenoxy, or benzyl, or b) one substituent from group a) and one or more substituents selected from halogen, C₁-C₄ alkyl, and C₁-C₄ alkylthio,

30 Y is H, C₁-C₄ alkanoyl, C₁-C₄ haloalkanoyl, or (C₁-C₄ alkoxy)carbonyl, and

R is H, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy, C₁-C₄ haloalkoxy, or phenyl(C₁-C₄ alkoxy)

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6 The method as recited in claim 5 wherein
X is a) phenyl, phenyl(C₁-C₂)alkoxy, or phenoxy, or
b) one substituent from group a) and one or more
substituents selected from halogen, C₁-C₂ alkyl, and C₁-C₂
5 alkylthio,

Y is H, C₁-C₄ alkanoyl, C₁-C₂ haloalkanoyl, or (C₁-C₂
alkoxy)carbonyl, and

R is H, C₁-C₄ alkyl, C₁-C₄ haloalkyl, C₁-C₄ alkoxy,
C₁-C₄ haloalkoxy, or phenyl(C₁-C₄ alkoxy)

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7 The method as recited in claim 6 wherein X is
phenylmethoxy, phenoxy, or phenyl and halogen or C₁-C₂
alkylthio, Y is hydrogen or C₁-C₂ haloalkanoyl, and R is
C₁-C₄ alkoxy or C₁-C₄ haloalkoxy

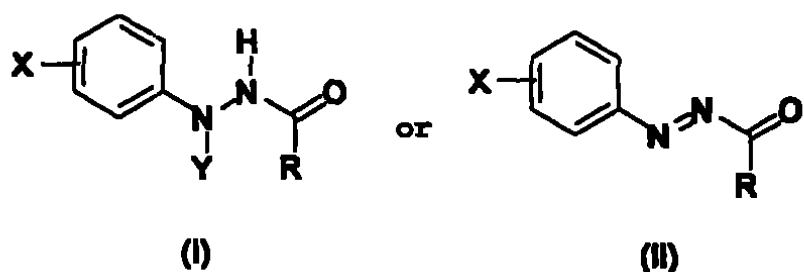
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8 The method as recited in claim 7 wherein X is
phenoxy, Y is hydrogen, and R is C₁-C₄ alkoxy

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A B S T R A C T

A method for controlling fungi using a
phenylhydrazine derivative compound of the formula



wherein

X is phenyl, phenylalkoxy, phenoxy, or benzyl, alone
or in combination with one or more halogen, alkyl, or
alkylthio,

Y is hydrogen, alkanoyl, haloalkanoyl, or alkoxy
carbonyl, and

R is hydrogen, alkyl, haloalkyl, alkoxy, haloalkoxy,
or phenylalkoxy

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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY	Atty Docket No 6381
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As a below named inventor, I hereby declare that.

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the invention entitled **METHOD FOR CONTROLLING FUNGI USING PHENYLHYDRAZINE DERIVATIVES**, which is described and claimed in the patent specification which

☒ (X) is attached hereto,

☐ () was filed on and accorded serial number ,

and for which invention Letters Patent are sought.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, Sec 1 56(a)

I hereby appoint the following attorneys and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith Daniel Reitenbach - Reg No 30,970, and Raymond D Thompson - Reg. No 30,695

Address all correspondence to Daniel Reitenbach Uniroyal Chemical Company, Inc World Headquarters Middlebury, Connecticut 06749	Direct telephone calls to Daniel Reitenbach Tel no (203) 573-4388 Fax no (203) 573-4430
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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Continued)	Atty Docket No 6381
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of the application or any patent issued thereon

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