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## N,N'-PHTHALYL HYDRAZINE FUNGICIDAL COMPOSITION

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3 Claims. (Cl. 167—33)

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This invention has for its object the production of a new group of superior fungitoxic materials, and methods for their use in protecting agricultural, organic and related articles from attack by fungi. This application is a division of co-pending application Serial No. 192,804 filed October 28, 1950, now abandoned.

We have found that N,N'-phthalylhydrazine and salts thereof possess unusual fungicidal properties. Alone, these materials are too powerful for safe application, but when suitably diluted and formulated as hereinafter described they are excellent fungicides. Such diluents function as surface-contacting agents and extenders.

By the term "fungicide" we mean to include not only the property of destroying fungi, but also the property of inhibiting the germination of the spores of the fungi.

One method of applying N,N'-phthalylhydrazine and its salts is in the form of a water suspension, wherein a surface active agent has been incorporated in sufficient amount to disperse and suspend the fungicide. Examples of such surface active agents which can be employed in forming dispersions of our fungicides include salts of the alkyl and alkylaryl sulfonates, such as du Pont MP–189 and Nacconol-NR, alkyl sulfates, such as Dreft, alkylamide sulfonates, such as Igepon-T, the alkylaryl polyether alcohols, such as Triton X–100, the fatty acid esters of polyhydric alcohols, such as Span, the ethylene oxide addition products of such esters, as for example Tween, and the addition products of long-chain mercaptans and ethylene oxide, such as Sharples' Non-Ionic–218. Still other surface active agents can be employed, the above merely constituting a representative list of the more common materials.

The solubility of N,N'-phthalylhydrazine in organic solvents is such that it can be applied advantageously in the form of solutions in this type of solvent, and for certain applications this method of application is preferred. For example, in treating cloth, leather, fur, felting or other fibrous articles it may be desirable to apply our fungicides dissolved in a volatile solvent. After use the volatile solvent evaporates leaving the fungicide impregnated throughout the surface of the article. Likewise, in applying our fungicides to smooth surfaces, as for example in treating

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wood surfaces for protection against fungus attack, a solution may be the most practical method for applying a protective film by brushing, spraying or dipping. The choice of an appropriate solvent is determined largely by the concentration of active ingredient which it is desired to employ, by the volatility required in a solvent, the spreading or flow characteristics thereof, and by the nature of the material being treated. Among the many organic solvents which can be employed as the carrier for our fungicides we can employ hydrocarbons, such as kerosene, benzene or toluene; ketones, such as acetone and methyl-ethyl ketone; chlorinated solvents, such as carbon tetrachloride, trichloro- and perchloro-ethylene; and esters, such as ethyl, butyl and amyl acetates; and alcohols, such as methanol, ethanol and isopropanol. Among the solvents which we prefer to employ are the Carbitols and Cellosolves, the former comprising in general the monoalkyl ethers of diethylene glycol and the latter the monoalkyl ethers of ethylene glycol. In addition, combinations of these various typical solvents can be employed whereby special volatility and viscosity characteristics can be imparted to our formulations.

In addition to the above-described methods of wet application of N,N'-phthalylhydrazines, we can prepare compositions in which our materials are extended in talc, clay or other solid diluents which impart a surface contacting effect. Such formulations have particular utility in the treatment of seeds, wherein an aqueous application may promote premature germination, or where a solvent application may damage the seed. For certain field crop applications we also prefer a dust formulation wherein a wet application might introduce certain secondary effects which are undesirable. Further specific examples of such typical inert solid carriers which can be employed as diluents in our dust formulations include fuller's earth, Pyrophillite, Attaclay and the Filtrols.

Further, we can employ a combination of the above methods of application of our fungicides. Thus, we can incorporate a surface-active agent or lubricant in our dust formulations, not only to ensure a uniform dry mixture, but also to enhance the spreading characteristics on application. Of particular utility for such formula-

tions are the alkyl or alkylaryl sulfonate detergents. Likewise, a solvent formulation can be employed along with water, or water and a surface-active agent. Such surface-active agents can be chosen, for example, from the types represented by Triton X–100, Sharples' Non-Ionic–218 or Tween. To illustrate, we dissolve N,N'-phthalylhydrazine in a solvent, such as ethyl acetate, along with a dispersant, and before application this concentrate is added to water, thereby producing a suspension of the fungicide in water, at the desired concentration for application.

In addition, to any of the above formulations we can incorporate an adherent or sticking agent or a humectant. Furthermore, the above formulations can be employed in admixture with other fungicidal materials or other biocides such as insecticides, larvicides, bactericides, vermicides, miticides, or with other materials which it is desired to apply along with our fungicide, such as for example herbicides or fertilizers.

In addition to the free N,N'-phthalylhydrazine, we can employ our fungicides in the form of salts. Thus, for example, the alkali metal salts, in particular the sodium and potassium salts, possess the characteristic of high water-solubility, and for some applications this is preferred. Likewise, the alkaline-earth metal salts, including the calcium, barium and magnesium salts, may be preferred for certain uses wherein a more limited water solubility is desired. Other metal salts can also be employed and can be chosen so as to impart not only a particular water solubility but also to enhance the fungitoxicity of the N,N'-phthalylhydrazine. Examples of such embodiments of the fungicides of our invention include the group I metal salts, as for example the copper and silver salts; the group II metals, in particular zinc and mercury; the group IV metals, as for example tin and lead. Other metal salts of N,N'-phthalylhydrazine which are particularly effective include the chromium, cobalt and iron salts thereof. One method of utilizing the salts of our fungicides comprises applying a water solution thereof to a fibrous or absorbent material to be protected, and thereafter depositing the free azinedione upon the fibers thereof by treatment with a mildly acidic material. One special technique which is particularly effective is to precipitate an aluminum "lake" of our fungicides upon fibrous materials, by methods which are well-known in the dye application art.

In addition to metal salts, N,N'-phthalylhydrazine forms salts with organic bases, the most common of which are the nitrogen bases, and in this form our azinediones are particularly effective. Examples of organic bases which are reacted with N,N'-phthalylhydrazine to form active fungicides include the alkylamines, such as methylamine, diethylamine, triethylamine, ethanolamine, diethanolamine, triethanolamine, ethylenediamine, morpholine, piperidine, pyridine, quinoline, n-butylamine, isoamylamine, dihexylamine, N-methyl - N - butylamine, triamylamine and benzylamine, and the arylamines, such as aniline, methylaniline, dimethylaniline, toluidine, N-methyltoluidine, xylidine, N-butylxylidine, α-naphthylamine, and β-naphthylamine. Likewise, ammonia itself forms ammonium salts with N,N'-phthalylhydrazide to form an effective, water-soluble fungicide.

We have illustrated the utility of N,N'-phthalylhydrazine and the metal salts thereof as fungitoxic materials by determining the concentration at which the germination of 50 per cent of the spores of each of the fungi *Alternaria oleracea* and *Sclerotinia fructicola* is inhibited. The former is responsible for the potato blight, while the latter causes peach rot. These fungi are representative of fungus types which are responsible for heavy crop damage. The ability to control these fungi is a reliable indication of the general applicability of our fungicides to protect these and other important agricultural crops. These tests were conducted as follows: 100 parts of N,N'-phthalylhydrazine was triturated with 1,000 parts of distilled water containing one part of the commercial dispersant Triton X–100. This standard suspension was thereupon further diluted with distilled water and the concentration at which one-half of the fungi contained in a drop of water on a microscope slide were prevented from sporilating was determined. With the insoluble metal salts as for example the barium, zinc, mercury, lead or cobalt salts, a similar procedure is employed, as well as with salts of most organic bases. With the soluble salts, as the sodium and potassium salts of N,N'-phthalylhydrazine and ammonium and soluble organic-base salts, it is only necessary to form a standard solution of the fungicide in water, and further dilute the solution to the minimum effective concentration. For example against *A. oleracea* the effective concentration of N,N'-phthalylhydrazine was less than 1 p. p. m. The salts are likewise effective at similar concentrations. Our fungicides are effective against *S. fructicola* at a concentration of less than 10 p. p. m. This standard slide-germination method is described by the Committee on Standardization of Fungicidal Tests of the American Phytopathological Society in "Phytopathology," 33, 627 (1943).

We have established that the fungicides of our invention are non-toxic to seeds and seedlings by incubating cucumber and rye seeds at a temperature of 25° C. in the dark for four and seven days, respectively, in Petri dishes containing a filter paper moistened with aqueous suspensions of our azinediones. Suspensions of our materials were prepared by dispersing one part of the N,N'-phthalylhydrazine or insoluble salt thereof, or dissolving one part of the soluble salts, in 10,000 parts of water containing 0.1 part of Santomerse-S, thus producing a formulation containing 100 p. p. m. of active ingredient. At the end of the incubation period we compared the growth of the primary root tip of the cucumber seed and the growth of the rye coleoptile with that obtained on seeds incubated with distilled water. We found no significant inhibition, compared with the controls, when germination proceeded in the presence of our fungicides. Germination of the treated seeds was as complete as the control.

It is important that a fungicidal composition does not cause damage to the leaves, stem, blossom, or fruit of a plant to which it is applied. When we dipped the entire leaf of each of corn, soybean, tomato, cucumber and cotton plants in a suspension of N,N'-phthalylhydrazine at a concentration of 10,000 p. p. m., we observed no effect on the so-treated plants or upon the leaves which were dipped. In like fashion, when leaves are dipped in suspensions or solutions of salts of our fungicides, no damage occurs to the plant. These dispersions were made according to the procedure of the previous example. Furthermore, each of these plants was totally sprayed with dispersions of our fungicides in water at a

concentration of 10,000 p. p. m. without any significant effect on the plant.

Listed below are several representative diseases of plants which can be controlled by our fungicidal materials and also the fungus organisms which are responsible for these phytopathological conditions.

DISEASES OF FRUITS

| | |
|---|---|
| Apple scab | *Venturia inaequalis* |
| Peach and cherry rots | *Sclerotinia fructicola* |
| Pear blight | *Erwinia amylovora* |
| Strawberry leaf spot | *Mycosphaerella fragaria* |
| Cherry leaf spot | *Coccomyces hiemalis* |
| Citrus scab | *Elsinoe fawcettic* |
| Citrus stem end rot | *Diaporthe citri* |

DISEASES OF GRAINS

| | |
|---|---|
| Wheat stem rust | *Puccinia gramminis* |
| Wheat leaf rust | *Puccinia triticina* |
| Oat crown rust | *Puccinia coronata* |
| Sweet corn smut | *Ustilago zeae* |
| Rice brown spot | *Helminthosporium oryzae* |
| Corn rot | *Diplodia zeae*, *Gibberella zeae*, *Fusarium moniliforme* |
| Oat smut | *Ustilago avenae*, *Ustilago levis* |

DISEASES OF TUBERS

| | |
|---|---|
| Sweet potato stem rot | *Fusarium batatis*, *Fusarium hyperoxysporum* |
| Potato late blight | *Phytophthora infestans* |
| Sugar beet leaf spot | *Cercospora beticola* |
| Sweet potato black rot | *Ceratostomella fimbriata* |
| Potato Rhizoctoniose | *Rhizoctonia solani* |
| Potato Scab | *Actinomyces scabies* |

MISCELLANEOUS VEGETABLE CROP DISEASES

| | |
|---|---|
| Tomato early blight | *Alternaria solani* |
| Pea root and stem rots | *Aphanomyces sp.*, *Fusarium sp.* |
| Tomato septoria blight | *Septoria lycopersici* |
| Peanut leaf spot | *Cercospora personata* |
| Celery late blight | *Septoria apii* |
| Cabbage black leg | *Phoma lingam* |
| Cucurbits down mildew | *Peronoplasmopara cubensis* |

MISCELLANEOUS

| | |
|---|---|
| Cotton wilt | *Fusarium vasinfectum* |
| Cotton root rot | *Phymatotrichum omnivorum* |
| Cotton blights and boll rot | *Rhizoctonia solani*, *Sclerotium bataticola*, *Diplodia gossypina* |
| Tobacco blue mold | *Peronospora tabacina* |
| Tobacco wild fire | *Phytomonas tabacum* |

As one example of a method of formulating a dust containing our fungicides, we ground 100 parts of N, N'-phthalylhydrazine with 1900 parts of talc such that the particles in the formulation were smaller than 80 mesh, and the concentration of active ingredient was 5 per cent. Likewise, when the salts of this material are ground with talc, similar dust formulations are produced.

We prepared oil-in-water emulsions of our fungicides as follows: a saturated solution of N, N'-phthalylhydrazine in kerosene was added, with agitation, to water containing a small amount of Triton X–100, thus obtaining a dispersion suitable for application as a spray. In a similar fashion a dispersion is made of the oil-soluble salts thereof. For the oil-insoluble, water-soluble salts we reverse the above procedure.

It is evident from the foregoing that our fungicides can be first formulated into a concentrate, wherein an inert diluent is admixed therewith, and finally diluted to an appropriate concentration for application with the same or different diluent. Such final formulation we prefer to employ between about 1 and 1000 p. p. m. of active ingredient. In general, from practical considerations, we prefer to prepare a concentrate containing up to approximately 50 weight per cent of our fungicides. If preferred, however, our fungicides can be diluted to application strength all at once. In either case, our fungicides when incorporated in the diluent are stable on storage and can be satisfactorily handled in either the diluted or concentrated state.



The fungicides of our invention also protect other materials besides plants and seeds. Examples of such materials, which are susceptible to attack by fungus organisms and which are protected by treatment with N,N'-phthalylhydrazine, or salts thereof, include wood, cloth fabrics, leather, fur, hair, feathers, felting painted or otherwise coated surfaces, and other articles of manufacture which comprise organic materials or are coated with such organic materials. Our fungicides can be applied to such materials as sprays, dusts, or dips, or can be brushed on, depending on the particular characteristics of the article or material which it is desired to protect from fungus attack. Furthermore, our fungicides are useful as soil disinfectants and can be applied directly thereto, thus providing protection to seeds, roots and emergent seedlings, or other material embedded in soil, such as for instance wood, cloth or other articles from soil-infesting fungi.

Other methods of employing the fungicidal compositions of our invention and other materials which can be protected from attack by fungus organisms will be apparent to those skilled in the art and the above specific examples are intended only to illustrate our invention. However, we do not intend that our invention be limited to these specific examples.

We claim:

1. A fungicidal composition consisting essentially of a material selected from the group consisting of N,N'-phthalylhydrazine, metallic salts thereof and salts thereof with organic nitrogen bases in amount less than about 50 per cent by weight, an inert diluent and a surface-active agent.

2. A fungicidal composition consisting essentially of a material selected from the group consisting of N,N'-phthalylhydrazine, metallic salts thereof and salts thereof with organic nitrogen bases in amount between about 1 and 1000 p. p. m., a diluent therefor and a surface-active agent.

3. The composition of claim 2 wherein the fungicidal ingredient is N,N'-phthalylhydrazine.

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