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SULFONYL ETHYLENE FUNGICIDES

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This invention relates to a new class of fungicidal compounds and more particularly to bis(organosulfonyl) ethylenes having especial utility as seed protectants.

A principal object of this invention is to provide a new class of fungicidal compositions. Another object is to provide a means of controlling fungi and especially a means of protecting seeds against the ravages of fungi. Still another object is to provide a new class of organic compounds.

It has now been discovered that the class of compounds known as bis(organosulfonyl) ethylenes possess outstanding fungicidal activity. Particularly remarkable are bis(alkylsulfonyl) ethylenes of the formula

$$RSO_2CH{=}CHSO_2R$$

where R is an alkyl group of 3 to 12 carbon atoms. By applying bis(organosulfonyl) ethylenes to the habitat of fungi, particularly to seeds before planting, very effective fungus control is obtained.

The bis(organosulfonyl) ethylenes which comprise the active ingredients of this invention can be represented by the general formula $R_1SO_2CR_2{=}CR_3SO_2R_4$, wherein R_1 and R_4 are organo groups, usually hydrocarbonaceous radicals of the alkyl, aryl, and aryl-substituted alkyl type, and R_2 and R_3 are organic radicals or hydrogen, usually the latter.

There are several variations in structure within the purview of the formula in the preceding paragraph, and all these structures are contemplated by the present invention.

The most common and most preferred variant of the structure $R_1SO_2CR_2{=}CR_3SO_2R_4$ is that in which

$$R_1{=}R_4{=}\text{alkyl}$$

or aryl hydrocarbonaceous radical, and

$$R_2{=}R_3{=}\text{hydrogen}$$

Examples of this type of compound in the aliphatic series include 1,2-bis(methylsulfonyl) ethylene; 1,2-bis(ethylsulfonyl) ethylene; 1,2-bis(n-propylsulfonyl) ethylene; 1,2-bis(isopropylsulfonyl) ethylene; 1,2-bis(n-butylsulfonyl) ethylene; 1,2-bis(isobutylsulfonyl) ethylene; 1,2-bis(t-butylsulfonyl) ethylene; 1,2-bis(amylsulfonyl) ethylene; 1,2-bis(hexylsulfonyl) ethylene; 1,2-bis(heptylsulfonyl) ethylene; 1,2-bis(octylsulfonyl) ethylene; 1,2-bis(nonylsulfonyl) ethylene; 1,2-bis(decylsulfonyl) ethylene; 1,2-bis(undecylsulfonyl) ethylene; and 1,2-bis(dodecylsulfonyl) ethylene or 1,2-bis(laurylsulfonyl) ethylene. An example in the aryl-substituted alkyl class is 1,2-bis(benzylsulfonyl) ethylene. In the aromatic series, wherein the aromatic constituent is a hydrocarbonaceous aryl radical, compounds within the scope of this invention include 1,2-bis(phenylsulfonyl) ethylene; 1,2-bis(tolylsulfonyl) ethylene, including 1,2-bis(o-tolylsulfonyl) ethylene, 1,2-bis(m-tolylsulfonyl) ethylene, and 1,2-bis(p-tolylsulfonyl) ethylene; 1,2-bis(biphenylsulfonyl) ethylene; and the like. When the aryl group is substituted, I may have 1,2-bis(nitrophenylsulfonyl) ethylene, including 1,2-bis(o-nitrophenylsulfonyl) ethylene, 1,2-bis(m-nitrophenylsulfonyl) ethylene, and 1,2-bis(p-nitrophenylsulfonyl) ethylene; 1,2-bis(halophenylsulfonyl ethylene, including 1,2-bis(chlorophenylsulfonyl) ethylene and 1,2-bis(bromophenylsulfonyl) ethylene; 1,2-bis(halonitrophenylsulfonyl) ethylene; 1,2-bis(aminophenylsulfonyl) ethylene; and the like.

This invention also contemplates bis(organosulfonyl) ethylenes wherein R_1 and R_4 differ. When they differ, they may be two alkyl groups, two aryl hydrocarbon groups, an alkyl and an aryl hydrocarbon group, etc. Examples of this type compound include 1-phenylsulfonyl-2-p-tolylsulfonyl ethylene; 1-phenylsulfonyl-2-p-nitrophenylsulfonyl ethylene; 1-methylsulfonyl-2-phenylsulfonyl ethylene; 1-hexylsulfonyl-2-m-tolylsulfonyl ethylene; and the like.

Finally, this invention contemplates those bis(organosulfonyl)ethylenes in which R_2 and R_3 are organic groups rather than hydrogen. Examples of this compound include 2,3-bis(methylsulfonyl) butene-2; 1,2-bis(p-tolylsulfonyl) butene-1; and the like.

It is to be remembered that cis-trans isomerism exists in this series of compounds and that the ordinary preparation yields mixtures of such isomers. However, it is possible to separate the cis from the trans isomer by the usual methods for such separation. My invention contemplates the use not only of the pure cis and trans isomers but also of cis-trans mixtures, as both the mixtures and the pure isomers possess fungicidal activity. An especially preferred modification of this invention comprises use of the trans isomers since, as will be shown below, in many cases they possess unexpectedly higher fungicidal activity than does the cis isomer or the mixture. When I use the term "trans isomer," I speak of the higher melting isomer, which generally has a lower solubility than the lower melting one. Although to the best of my knowledge and belief the higher melting isomer is the trans isomer, I do not wish to be bound by this, and throughout the specification, when I speak of trans, I am referring to the higher melting of the two geometric isomers of a given bis(organosulfonyl) ethylene.

Also within the scope of this invention I have discovered a new class of chemical compounds possessing extremely high seed protectant effectiveness. This new class of compounds comprises the bis(alkylsulfonyl) ethylenes of the formula $RSO_2CH{=}CHSO_2R$, where R is an alkyl group of 3 to 12 carbon atoms. Examples of this new class of compounds include trans 1,2-bis(n-propylsulfonyl) ethylene; cis 1,2-bis(isopropylsulfonyl) ethylene; trans 1,2-bis(n-butylsulfonyl) ethylene; cis 1,2-bis(isobutylsulfonyl) ethylene; trans 1,2-bis(t-butylsulfonyl) ethylene; cis 1,2-bis(amylsulfonyl) ethylene; trans 1,2-bis(hexylsulfonyl) ethylene; cis 1,2-bis(heptylsulfonyl) ethylene; trans 1,2-bis(octylsulfonyl) ethylene; cis 1,2-bis(nonylsulfonyl) ethylene; trans 1,2-bis(decylsulfonyl) ethylene; cis 1,2-bis(undecylsulfonyl) ethylene; trans 1,2-bis(laurylsulfonyl) ethylene; and cis 1,2-bis(laurylsulfonyl) ethylene. As will be demonstrated below, this new class of compounds possesses seed protectant fungicidal activity which is unexpectedly even higher than that of the other sulfonyl ethylenes within the scope of this invention.

The compounds of this invention can be conveniently prepared by reaction of an olefin having halogen atoms on adjacent olefinically unsaturated carbon atoms with a mercaptan or mixtures of mercaptans, followed by oxidation of the corresponding bis(organomercaptyl) ethylene to form the sulfone. When the desired product is one in which R_2 and R_3 equal hydrogen, then the most convenient starting olefin is 1,2-dichloroethylene or, in general, 1,2-dihaloethylene, where the halogen is most commonly chlorine or bromine or one of each. When the desired product is one in which R_2 and/or R_3 is other than hydrogen, other olefins should be used as starting materials. For example, use of 1,2-dichlorobutene-1 and 2,3-dichlorobutene-2 will result in products in which R_2 and/or R_3 are alkyl. When R_1 and R_4 are to be the same in the desired product, then 2 moles

of a mercaptan are reacted with 1 mole of the halogenated olefin, whereas if R_1 and R_4 are to be different, then 1 mole of a mercaptan corresponding to R_1 is reacted with the olefin and the resulting product is reacted with a mercaptan corresponding to R_4.

As an example of a preferred type process of this invention, reaction of 1,2-dichloroethylene with ethyl mercaptan yields 1,2-bis(ethylmercapto) ethylene, which upon treatment with hydrogen peroxide yields bis(ethylsulfonyl) ethylene according to the following equations:

$$2C_2H_5SH+2KOH+ClCH=CHCl\rightarrow C_2H_5SCH=CHSC_2H_5+2KCl+2H_2O$$

$$C_2H_5SCH=CHSC_2H_5 + 4H_2O_2 \xrightarrow{HO} C_2H_5SO_2CH=CHSO_2C_2H_5 + 4H_2O$$

In addition to hydrogen peroxide, other oxidizing agents, such as potassium permanganate, sodium hypochlorite, chromic oxide, dilute nitric acid, and even electrolytic oxidation, can be used. Particularly in the aromatic series the halogenated olefin may be reacted directly with a salt of a sulfinic acid to yield the bias(organosulfonyl) ethylene directly.

Typical procedures for preparation of many of the compounds of this invention are illustrated in the following examples.

Example I

1,2-bis(ethylmercapto) ethylene.—Potassium hydroxide (86 parts) was dissolved in 790 parts of 95 percent ethanol, and 62 parts of ethyl mercaptan added all at once. A solution of 48.5 parts of cis 1,2-dichloroethylene in 40 parts of ethanol was then added with stirring during 1¼ hours while warming the mixture to reflux. During the addition and later, the system was vented only through two lead acetate traps and a column of charcoal impregnated with copper sulfate, all in series. Stirring and refluxing were continued for four hours more, and then the mixture was allowed to stand overnight. The precipitated salt was then filtered and solvent distilled at one atmosphere to reduce the volume by 60 percent. Dilution with several volumes of water precipitated an oil which was taken up in benzene and washed with water until the washings were neutral (four times). After drying over calcium chloride, distillation yielded 45.3 parts (61 percent) of 1,2-bis(ethylmercapto) ethylene as a nearly colorless oil of B.P. 91–94° C. at 5 mm. A forerun boiling at 84–91° C. at 5 mm. was rejected.

1,2-bis(ethylsulfonyl) ethylene.—1,2-bis(ethylmercapto) ethylene (45.3 parts) was added with stirring during one hour to a mixture of 170 parts of 30 percent hydrogen peroxide and 262 parts of acetic acid, keeping the temperature at 20–30° C. with external cooling. Stirring at this temperature was then continued for three hours, after which the mixture was allowed to stand overnight. The solvent was then removed by distillation at reduced pressure at 60° C. The residual acetic acid was then removed by vacuum drying at room temperature to leave a residue of colorless crystals weighing 64 parts (100 percent), M.P. 82–87° C. The broad M.P. is believed due to the presence of a mixture of the cis and trans isomers. Fromm and Landmann, Ber. 56, 2290 (1923), report the M.P. to be 88° C.

Example II

1,2-bis(n-propylmercapto) ethylene.—A solution of 80 parts of n-propyl mercaptan, 52 parts of cis 1,2-dichloroethylene, and 75 parts of potassium hydroxide in 800 parts of ethanol was heated under reflux for two hours. The cooled reaction mixture was filtered to remove precipitated potassium chloride and the volume of the filtrate reduced by distillation. The residue was diluted with several volume of water, the oily layer separated, and the aqueous phase extracted twice with benzene. The combined extracts were washed with water, dried over calcium chloride, and the benzene was removed by distillation. The residue was distilled under reduced pressure, giving 60.4 parts (65 percent) of 1,2-bis(n-propylmercapto) ethylene as a light amber liquid with a mild odor, B.P. 134–142° C. at 18 mm. A cut boiling at a constant temperature of 141° C. at 18 mm. had the following analysis. Calculated for $C_8H_{16}S_2$: C, 54.5; H, 9.09; S, 36.4. Found: C, 54.6; H, 9.23; S, 36.7.

Example III

Cis and trans 1,2-bis(n-proplysulfonyl) ethylene.—Sixty-three parts of 30 percent hydrogen peroxide and 52 parts of glacial acetic acid were heated to 50° C. and 21.8 parts of 1,2-bis(n-propylmercapto) ethylene added dropwise. The temperature was allowed to rise to 90° C. and was held there by external cooling. After the addition was complete the solution was heated at 80–90° C. for one hour and allowed to stand overnight. The reaction mixture was diluted with an equal volume of water and cooled in an ice-salt bath for several hours. The product was filtered, washed with ice water, and dried over potassium hydroxide, in vacuo, giving 14.7 parts (49 percent) of 1,2-bis(n-propylsulfonyl) ethylene as colorless crystals. This product was a mixture of cis and trans isomers, melting over a wide range (45–135° C.). *Analysis.*—Calculated for $C_8H_{16}S_2O_4$: S, 26.6. Found: S, 26.9. Crystallization from water-ethanol gave 3.4 parts (11 percent) of the trans isomer, colorless leaves, M.P. 153–154° C. *Analysis.*—Calculated: C, 40.0; H, 6.67; S, 26.6. Found: C, 40.1; H, 6.79; S, 27.2. The cis isomer separated from the mother liquors upon cooling in the refrigerator overnight. Yield, 7.0 parts (23 percent) colorless leaves, M.P. 42–44° C. *Analysis.*—Found: C, 39.5; H, 6.79; S, 27.0.

Example IV

1,2-bis(2-propylsulfonyl) ethylene.—1,2-bis(2-propylmercapto) ethene (35 parts) prepared in a manner similar to the mercaptoethylenes of the previous examples was added dropwise to a stirred solution of 102 parts of 30 percent hydrogen peroxide in 95 parts of glacial acetic acid. Application of external cooling was necessary to prevent the temperature from rising above 80–90° C. When the heat of reaction had subsided, the solution was boiled 30 minutes and allowed to stand overnight. Upon addition of water and cooling in ice, the product precipitated and was filtered and washed with ice-cold water, giving 38 parts (80 percent) of 1,2-bis(isopropylsulfonyl) ethylene as white flakes which after crystallization from water-ethanol melted at 132.5–133° C. *Analysis.*—Calculated for $C_8H_{16}O_4S_2$: C, 40.0; H, 6.67; S, 26.6. Found: C, 39.9; H, 6.75; S, 26.9.

Example V

1,2 - bis(p - tolylsulfonyl) ethylene.—In a reactor equipped with an agitator and reflux condenser were placed 130 parts of glacial acetic acid and 28.3 parts of 1,2-bis(p-tolylmercapto) ethylene. The mixture was refluxed until the solution was clear, and then 93.8 parts of 30 percent hydrogen peroxide was added. The mixture was refluxed for 2 hours, cooled, and the product, 1,2-bis-(p-tolylsulfonyl) ethylene, collected by filtration. Yield, 33.4 parts (71 percent); M.P. 139–144° C. (Truce and McManimie, J. Am. Chem. Soc. 75, 1672 (1953), report 147–153° C.)

Example VI

1,2 - bis(methylsulfonyl) ethylene.—1,2 - bis(methylmercapto) ethene (38.5 parts) was added with stirring to a mixture of 170 parts of 30 percent aqueous hydrogen peroxide and 260 parts of acetic acid, keeping the temperature at 20–30° C. with external cooling as necessary. The addition required ½ hour, after which the mixture was allowed to stand overnight. The solvent was then distilled at reduced pressure by heating the mixture to not over 60° C. The residual oil was caused to crystallize by treatment with diethyl ether. The crude

product then consisted of 55 parts (93 percent) of 1,2-bis(methylsulfonyl) ethylene as a tan solid melting at 60–75° C. This product was recrystallized from 240 parts of ethanol, it being found necessary to filter while hot to remove a small amount of insoluble material. This yielded 34 parts (57 percent) of the product as colorless crystals, M.P. 74–80° C. The broad M.P. and the presence of a distinctly less soluble fraction indicates the existence of both the cis and trans isomers in the product. Two parts of the product were recrystallized once more from ethanol to yield one part of the more soluble—presumably cis—fraction melting at 92–95° C. *Analysis.*—Calculated for $C_4H_8O_4S_2$: C, 26.1; H, 4.35; S, 34.8. Found: C, 25.9; H, 4.63; S, 34.9.

Example VII

1,2-bis(laurylsulfonyl) ethylene.—This compound was prepared from 1,2-bis(laurylmercapto) ethene and hydrogen peroxide as in the foregoing examples. Yield, 71.3 percent; M.P. 80–83° C. *Analysis.*—Calculated for $C_{26}H_{52}O_4S_2$: S, 13.0 percent. Found: S, 12.3 percent.

Example VIII

1,2-bis(n-octylsulfonyl) ethylene.—This compound was prepared from 1,2-bis(n-octylmercapto) ethene and hydrogen peroxide as in the foregoing examples. Yield, 89 percent; M.P. 83.8° C. *Analysis.*—Calculated for $C_{18}H_{36}O_4S_2$: C, 56.8 percent; H, 9.46 percent. Found: C, 56.6 percent; H, 9.53 percent.

Example IX

In a reactor equipped with liquid feed means, mechanical agitation, and a reflux condenser was placed a solution of 20 parts of cis 1,2-bis(p-tolylsulfonyl) ethylene in 150 parts of chloroform. To this solution was added slowly about 3 parts of bromine. The bromine color persisted on standing. After addition was complete the mixture was irradiated with a sun lamp, whereupon the bromine color was rapidly dissipated with formation of a precipitate. The precipitate was cooled and washed with chloroform to give 12.5 parts of trans 1,2-bis-(p-tolylsulfonyl) ethylene as colorless crystals, M.P. 225–227° C. (lit. value, 228° C.). *Analysis.*—Calculated for $C_{15}H_{16}S_2O_4$: S, 19.1 percent. Found: S, 19.1 percent. Evaporation of the filtrate gave an additional 6.2 parts of the trans product melting at 210–218° C.

Example X

1,2-bis(n-butylsulfonyl) ethylene.—In a reactor were placed 17.0 parts of 1,2-bis(n-butylmercapto) ethane dissolved in 75 parts of a 1:1 mixture of glacial acetic acid and acetic anhydride. The solution was cooled externally and 54.9 parts of 30 percent H_2O_2 added in two hours, keeping the temperature between 20 and 40° C. At the completion of the addition the solution was allowed to stand at room temperature for four days.

At the end of this time the solution had separated into two layers. These were fed into ice water with agitation. The product was collected by filtration, washed with H_2O, and dried under vacuum at room temperature over KOH. Recrystallization from water and MeOH gave 15.0 parts (79.7 percent) of 1,2-bis(n-butylsulfonyl) ethylene, M.P. 61–63° C. *Analysis.*—Calculated for $C_{10}H_{20}S_2O_4$: C, 44.8 percent; H, 7.45 percent. Found: C, 44.7 percent; H, 7.34 percent.

Example XI

1,2-bis(n-amylsulfonyl) ethylene.—In a reactor were placed 3 parts of 1,2-bis(n-amylmercapto) ethylene dissolved in 75 parts of a 1:1 mixture of acetic acid and acetic anhydride. The solution was cooled externally and 52.0 parts of 30 percent H_2O_2 added in two hours, keeping the temperature between 20 and 40° C. At the completion of the addition the solution was allowed to stand at room temperature for four days. Yield (after recrystallizing from acetic acid-H_2O, then twice from MeOH—H_2O), 16.9 parts (72.7 percent) of 1,2-bis(n-amylsulfonyl ethylene; M.P. 51–55° C. *Analysis.*—Calculated for $C_{12}H_{24}O_4S_2$: S, 21.6 percent. Found S, 21.8 percent.

Example XII

1,2-bis(p-nitrophenylsulfonyl) ethylene-dibenzene adduct

$$p\text{-}(O_2N)C_6H_4SCH{=}CHSC_6H_4(NO_2)p + 4H_2O_2 \xrightarrow{C_6H_6} p\text{-}(O_2N)C_6H_5SO_2CH{=}CHSO_2C_6H_4(NO_2)p(C_6H_6)_2$$

To a stirred solution of 55 parts of 30 percent hydrogen peroxide in 210 parts of glacial acetic acid heated to 90° C. was added portionwise 35 parts of powdered 1,2-bis(p-nitrophenylmercapto) ethylene at such a rate that the temperature did not rise above 96° C. This required 10 minutes, and no external heating or cooling is necessary. The mixture was then heated under reflux for 10 minutes, cooled, filtered, and the filtrate poured into 500 parts of ice and 1000 parts of water containing about 2 parts of sodium chloride. The yellow precipitate was filtered, washed with ice water, and dried in vacuo at room temperature. The crude product was extracted for several hours with 800 parts of benzene in a continuous liquid-solid extractor. The benzene extract was boiled with charcoal, filtered, and 480 parts of benzene removed by distillation. The product, 1,2-bis(p-nitrophenylsulfonyl) ethylene containing 2 molecules of benzene of crystallization, crystallized from the cooled benzene solution. Yield, 22 parts (38 percent) yellow plates; M.P. 148–153° C. (decomposes rapidly above about 100° C.). Crystallization from benzene raised the M.P. to 150–153° C. *Analysis.*—Calculated for $C_{26}H_{22}N_2O_8S_2$: N, 5.06; S, 11.6. Found: N, 5.11; S, 11.7.

For maximum effectiveness the compounds of the present invention are ordinarily admixed in fungicidally effective amount with a conditioning agent of the type commonly referred to as pest control adjuvant or modifier. Such conditioning agents are also known as surface-active agents, dispersing agents, dispersants, and sometimes as surface-active dispersing agents. In order to provide formulations particularly adapted for ready and efficient application to pests using conventional equipment, such formulations comprise those of both the liquid and solid types. Such adjuvants have the effect of requiring only minute quantities of the above defined compounds in some formulations to obtain effective protection. A further advantage of so extending these compounds is to permit field application by methods readily employed and still obtain effectively complete coverage of the material being protected.

The formulations of this invention, therefore, comprise the hereinabove defined pesticidally active ingredient and a suitable material as a dispersant or conditioning agent therefor. It is not intended that this invention be limited to any specific proportions of active ingredient and adjuvant. The important feature of the invention is to provide a conditioning agent such that upon the preparation of a formulation of such concentration as appropriate for application, the conditioning agent will be present to provide the proper type of contact with the material being protected. Thus, in one embodiment the conditioning agent can comprise a dispersing agent or surface-active agent such as a detergent, a soap, or other substance tending to lower the surface-tension of water. Such a formulation may then comprise the active ingredient in combination with a minor proportion of the surface-active agent. Such a concentrate formulation is of practical merit because of its concentrated form and ease of transportation, storage, and the like. Such a concentrate formulation lends itself directly to further dilution with the carrier without resorting to complicated mixing and blending procedures. Thus, such a formulation can be directly suspended in water or can be further diluted with an oil

which upon mixing with water thereby forms an oil-in-water emulsion containing the active ingredient. One further example of the utility of such a formulation comprises the preparation by further dilution with a solid carrier of a wettable powder which upon admixture with water prior to application forms a dispersion of the active ingredient and the solid carrier in water. In such concentrate formulations the amount of active ingredient varies between 5 and 99.9 percent of the whole.

It is also intended that the term "conditioning agent" include solid carriers of the type of talc, pyrophyllite, Attaclay, kieselguhr, chalk, diatomaceous earth, and the like; and various mineral powders, such as calcium carbonate and the like, which act as a dispersant, as a carrier, and in some instances perform the function of a surface-active agent.

One method of applying these fungicidies is in the form of a water suspension. To obtain a fungicidally active aqueous suspension, I preferably employ a surface-active agent in sufficient amount to disperse and suspend the pesticidal agent. Examples of such surface-active agents which can be employed in forming dispersions include metal salts of the alkyl and alkylaryl sulfonates, such as the sodium salt; alkyl sulfates; alkylamide sulfonates, including fatty methyl taurides; the alkylaryl polyether alcohols; the fatty acid esters of polyhydric alcohols; the ethylene oxide addition products of such esters, as, for example, a hexitol product; and the addition products of long chain mercaptans and ethylene oxide. Still other surface-active agents can be employed, the above merely showing a representative list of the more common materials.

In the examples which follow, all parts are parts by weight.

Example XIII

A formulation of trans bis(n-propylsulfonyl) ethylene is prepared by adding with vigorous agitation 10 parts of this material to 1000 parts of water containing one part of an ethylene oxide addition product of hexitol. This concentrated dispersion is further diluted 1000 times by the addition of water to obtain a formulation of suitable concentration for application. Thus, the resulting dispersion contains 10 p.p.m. of my fungicide in the water dispersion.

The solubility of the active ingredients of this invention is organic solvents, furthermore, in such they can be applied advantageously in the form of solution in this type of solvent, and for certain uses this method of application is preferred. For example, in treating cloth, leather, or other fibrous articles, it is sometimes preferred to apply the fungicides dissolved in a volatile solvent. After use the volatile solvent evaporates, leaving the fungicidal agent impregnated throughout the surface of the article and in the dispersed form which has been found to be most advantageous. Likewise, in applying the fungicide to smooth surfaces, as, for example, in treating wood or other surfaces, 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 ingredients 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 the fungicide, I use hydrocarbons, such as benzene, xylene, or toluene; ketones, such as acetone, methylethyl ketone, and cyclohexanone; chlorinated solvents, such as carbon tetrachloride, trichloro- and perchloroethylene; esters, such as ethyl, butyl, and amyl acetates; and alcohols, such as ethanol, isopropanol, and amyl alcohols. Other solvents which are employed 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 the formulations.

Example XIV

A solution of 5 parts of bis(p-nitrophenylsulfonyl) ethylene in 250 parts of cyclohexanone is prepared by stirring the two constituents for a period of 2 minutes at a temperature of about 25° C. This concentrated solution, suitable for storage or transportation, is further diluted with kerosene to form a final dilution of 50 p.p.m. suitable for application.

A preferred formulation of the active ingredient fungicide of this invention comprises a wettable powder. In preparing wettable powders several formulation procedures are possible. Thus, it is one intention of this invention to provide compositions comprising the active ingredient defined herein in combination with a minor amount of a surface-active agent. Such surface-active agent can be chosen, for example, from among those mentioned above in connection with aqueous dispersions. Still other surface-active agents can be employed, the above merely showing a representative list of the more common materials. Such formulations can be readily admixed with a dust carrier. Formulations thus formed then comprise the active ingredient of this invention, a surface-active agent, and the inert carrier. Among the inert carriers which can be employed in thus preparing wettable powders are, for example, soybean flour, tobacco flour, walnut shell flour, wood flour, sulfur, tripolite, diatomaceous earth, calcium lime, magnesium lime, calcite, dolomite, gypsum, mica, talc, pyrophillite, montmorillonite, kaolinite, attapulgite, apatite, and pumice. In preparing such concentrated wettable powders it is preferred to employ between about 0.1 and 95 percent of the surface-active agent based upon the total amount of surface-active agent and active ingredient, and up to 85 percent of the inert carrier based upon the total amount of the formulation. Such formulations provide the advantage of permitting storage and transportataion of the fungicide and permit further dilution by simple admixture with water at the time of application. Thus, within the scope of this invention is also contemplated finished formulations for direct application comprising the fungicides as defined herein, surface-active agents as illustrated above, and inert solid carriers as likewise illustrated above, all suspended in water. Such finished formulations, depending upon the application in mind, can include between about 0.1 and 10,000 p.p.m. of fungicide. A preferred range for agricultural application is between 0.1 and 2,000 p.p.m. Typical formulations of such wettable powders of this invention are illustrated in the following examples, wherein an active ingredient of this invention is employed as the fungicide.

Example XV

A mixture of 100 parts of bis(laurylsulfonyl) ethylene, 1000 parts of pyrophyllite, and 0.1 part of sodium keryl sulfonate is intimately co-mingled in an L-shaped blender. The 10 percent wettable powder thus prepared produces a satisfactory water suspension when 11 parts are stirred into sufficient water to produce a suspension containing 100 p.p.m. active ingredient.

In addition to the above described methods of wet application of the active ingredient of this invention, compositions can be prepared in which the material is extended in talc, clay, or other solid diluents. Such carriers perform the conditioning agent function as contact agents. Further specific examples of such typical inert solid carriers which can be employed as diluents in the dust formulations include fuller's earth, pyrophyllite, Attaclay, and the Filtrols.

Example XVI

A dust formulation of the fungicide is prepared as follows: One part of bis(methylsulfonyl) ethylene is placed in a ball mill with 100 parts of fuller's earth. This mix-

ture is milled for a period of one hour and screened to collect a fraction passing a 100-mesh sieve. This one percent by weight formulation can be applied directly or further diluted. A further dilution is made by repeating the above procedure with an additional 100 parts of fuller's earth per part of the first-obtained mixture.

For certain applications it is preferred to employ the fungicide in the form of oil-in-water emulsions. Thus, a concentrate of the fungicidal agent is prepared in a water-insoluble solvent, and this solution is then dispersed or emulsified in water containing a surface-active agent. Typical examples of such solvents include hydrocarbons, such as kerosene, benzene, or naphtha; higher alcohols, such as butanol, oleyl alcohol, or ethers and esters thereof; and chlorinated solvents, such as perchloroethylene and trichloroethylene.

Example XVII

An oil-in-water emulsion is prepared by dissolving 10 parts of bis(phenylsulfonyl) ethylene in 1000 parts of kerosene. This solution is dispersed with vigorous agitation in water containing 1 part of fatty methyl tauride to provide a dispersion containing 10 p.p.m. of active agent.

In addition I have found that I can incorporate an adherent or sticking agent, such as vegetable oils, naturally occurring gums, and other adhesives, in my active ingredient formulations. Likewise, I can employ humectants in my formulations. Furthermore, these formulations can be employed in admixture with other pesticidal materials or other biocides, such as insecticides, larvicides, bactericides, vermicides, miticides, other fungicides, or with other materials which it is desired to apply along with my fungicides, including mixtures of my active ingredients.

The fungicidal effectiveness of my new compounds is illustrated by the following results, wherein the active ingredients are shown to be effective fungicides against *Alternaria oleracea* and *Sclerotinia fructicola*. For this purpose a suspension of 100 parts of the bis(organosulfonyl) ethylene in 1000 parts of distilled water containing a small amount of a commercial dispersant, hexitol-ethylene oxide adduct, was prepared. This suspension was tested and further diluted with distilled water until the concentration of the active ingredient which would just prevent one-half of the fungi named above from sporulating, as observed in a drop of water on a microscope slide, was determined.

Compound	Concentration, p.p.m., for LD_{50} Against Fungus	
	A.o.	*S.f.*
Trans bis(n-propylsulfonyl) ethylene	0.5	5
Cis bis(n-propylsulfonyl) ethlene	5	5
Bis(n-butylsulfonyl) ethylene	5	5
Bis(n-amylsulfonyl) ethylene	0.5	0.5
Cis bis(p-tolylsulfonyl) ethylene	5	0.5
Bis(m-tolylsulfonyl) ethylene	0.5	0.5
Bis(p-nitrophenylsulfonyl) ethylene	5	0.5

The fungicidal activity of my compounds is further demonstrated by their effectiveness against tomato foliage disease. The tomato foilage disease test measures the percent control of late blight fungus, *Phytophthora infestans*. In the primary screen the chemicals are evaluated at concentrations of 2000 and 400 p.p.m. Tomato plants are sprayed with the test formulation, allowed to dry, and along with untreated controls are sprayed with a spore suspension of sporangia of *Phytophthora infestans*. The plants are held in a saturated atmosphere for 24 hours at 70° F. for early blight and 60° F. for late blight to permit spore germination and infection before removal to the greenhouse. After 2 to 4 days lesion counts are made on the three uppermost fully expanded leaves. Compounds giving 85 percent disease control or better against one or both disease-causing organisms at 400 p.p.m. are entered into secondary screening at dosages of 400, 80, 16, and 3.2 p.p.m. test chemical. For advanced evaluation the dosages are adjusted to the effectiveness of the test compound. This test method is a modification of that described by McCallan and Wellman (contrib. Boyce Thompson, 13 (3): 93–134. July-September 1943). The ED_{95} of typical compounds of this invention against the late blight fungus is bis(n-butylsulfonyl) ethylene, 50; bis(n-amylsulfonyl) ethylene, 60; and bis (p-tolylsulfonyl) ethylene (mixture of cis and trans), less than 16.

As mentioned above, particularly outstanding results in seed protection are obtained when the bis(organosulfonyl) ethylene used is one of the formula

$$RSO_2CH{=}CHSO_2R$$

where R is an alkyl group having 3 to 12 carbon atoms. In fact, this new class of compounds represent the most potent group of organic seed protectants known to date. This is shown especially by the following data, wherein the effectiveness of these materials as pea seed protectants was determined. In this test, pea seeds, Perfection variety, were uniformly coated with bis(organosulfonyl) ethylene by rolling mixtures of the seed and fungicide in screwcap bottles on high speed rollers. The dosage level was varied by using (1) undiluted chemical and (2) uniform mixtures of the test chemical and Homer clay. The treated pea seeds along with untreated controls and a reference standard were planted in soil contaminated with damping-off fungi. Untreated seeds were also planted in sterile soil as a control. After 14 days the percent emergence was recorded. The following are the results. With bis(ethylsulfonyl) ethylene and bis(methylsulfonyl) ethylene which do not have alkyl groups of 3 to 12 carbon atoms, the percent protection obtained at a concentration of the active ingredient of 0.48 percent was only 52 and 2 respectively. On the other hand, with bis(alkylsulfonyl) ethylenes whose alkyl groups contain 3 to 12 carbon atoms, the percentage protection obtained at an active ingredient concentration of 0.48 percent was as follows: trans bis(n-propylsulfonyl) ethylene, 96; bis(n-butylsulfonyl) ethylene, 92; and cis bis(n-propylsulfonyl) ethylene, 90. Furthermore, the activity of bis(alkylsulfonyl) ethylene whose alkyl groups have 3 to 12 carbon atoms as seed protections holds up when the concentration of the active ingredient is drastically reduced. For example, at a concentration of only 0.03 percent of active ingredient the percent protection given by bis(n-butylsulfonyl) ethylene was still 75, and concentrations of only 0.009 percent of trans bis(n-propylsulfonyl) ethylene gave 90 percent protection, while the same concentration of bis(isopropylsulfonyl) ethylene gave 58 percent protection. Even at the extremely minute concentration of 0.001 percent, trans bis(n-propylsulfonyl) ethylene gave 40 percent protection in this test.

Good seed protectant results are obtained with bis(n-octylsulfonyl) ethylene and bis(laurylsulfonyl) ethylene as well as other bis(alkylsulfonyl) ethylenes whose alkyl group contains 6 to 12 carbon atoms.

I claim:

1. As a new composition of matter, a bis(alkylsulfonyl) ethylene of the formula $RSO_2CH{=}CHSO_2R$, where R is an alkyl group of 2 to 12 carbon atoms and wherein the compound has the trans configuration.

2. Trans bis(n-propylsulfonyl) ethylene.

3. Trans bis(ethylsulfonyl) ethylene.

4. A compound of the formula $RSO_2CH{=}CHSO_2R$ where R is an alkyl group of 3 to 12 carbon atoms.

5. A fungicidal composition comprising a bis(organosulfonyl) ethylene of the formula $Q_1SO_2CH{=}CHSO_2Q_2$, wherein Q_1 and Q_2 are selected from the group consisting of alkyl having one to 12 carbon atoms, phenyl, biphenyl, benzyl, lower alkyl phenyl, chlorophenyl, bromophenyl and nitrophenyl together with a surface-active agent.

6. A fungicidal composition comprising a bis(alkylsulfonyl) ethylene of the formula $RS_2CH=CHSO_2R$, where R is an alkyl group of 3 to 12 carbon atoms, together with a surface-active agent.

7. Trans bis(n-propylsulfonyl) ethylene, together with a surface active agent.

8. Trans bis(ethylsulfonyl) ethylene and a contact agent from the group consisting of talc, clay, calcium carbonate and diatomaceous earth.

9. Trans bis(n-propylsulfonyl) ethylene and a contact agent from the group consisting of talc, clay, calcium carbonate and diatomaceous earth.

10. Trans bis(ethylsulfonyl) ethylene together with a surface active agent.

11. A method of controlling fungi, comprising applying to the material to be protected a bis(organosulfonyl) ethylene of the formula $Q_1SO_2CH=CHSO_2Q_2$, wherein Q_1 and Q_2 are selected from the group consisting of alkyl having one to 12 carbon atoms, phenyl, biphenyl, benzyl, lower alkyl phenyl, chlorophenyl, bromophenyl and nitrophenyl.

12. A method of protecting seeds from the ravages of fungi which comprises applyin to the seeds a bis(organosulfonyl) ethylene of the formula $Q_1SO_2CH=CHSO_2Q_2$, wherein Q_1 and Q_2 are selected from the group consisting of alkyl having one to 12 carbon atoms, phenyl, biphenyl, benzyl, lower alkyl phenyl, chlorophenyl, bromophenyl and nitrophenyl.

13. A method of protecting seeds from the ravages of fungi which comprises applying to the seeds a bis(alkylsulfonyl) ethylene of the formula $RSO_2CH=CHSO_2R$, where R is an alkyl group of 2 to 12 carbon atoms.

14. A method of controlling fungi comprising applying to the material to be protected bis(alkylsulfonyl) ethylene of the formula $RSO_2CH=CHSO_2R$, where R is an alkyl group of 3 to 12 carbon atoms.

15. A method of protecting seeds from the ravages of fungi which comprise applying to the seeds trans bis(n-propylsulfonyl) ethylene.

16. A method of controlling fungi, comprising applying to the material to be protected a compound of the formula $RSO_2CH=CHSO_2R$ where R is an alkyl group of 1 to 12 carbon atoms.

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