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3,102,070

MITICIDAL COMPOSITIONS

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This invention concerns pesticidal compositions which contain 1,1-bis(halophenyl)-2,2,2-trichloroethanol dissolved in an alkyl oleate in which the alkyl group contains one to two carbon atoms.

Pesticides, such as insecticides and miticides, are commonly formulated as emulsion concentrates and wettable powders for spray purposes, as dusts, and as aerosols. In the control of mites on agricultural and horticultural crops, it is common to apply emulsion concentrates or wettable powders in aqueous sprays. A particularly effective miticide for use in such sprays is 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethanol. It is usual practice to use this agent in conjunction with other types of pesticidal agents. For this purpose emulsion concentrates or wettable powders of these other agents are used in the same aqueous mixture as this miticide.

Often when this is done there is incompatibility. This incompatibility usually manifests itself in the formation of agglomerates or curds. This phenomenon is commonly known as "greasing out." The curdy or clabber-like material often accumulates at the surface of the spray mixture or on the sides of the spray tank and it may clog screens. Since it is not readily redispersed into the spray liquid, it is rendered unavailable for spray purposes. It is also conceivable that this type of incompatibility could occur on a leaf surface as well as in a spray tank when at least two pesticides are applied to leaf surfaces.

There are other situations wherein the pesticidal formulations of the art are reduced in effectiveness as when climatic conditions, such as low temperature, prevent the pesticidal formulations from acting in their optimum manner.

In the cold, for example, the 1,1-bis(halophenyl)-2,2,2-trichloroethanols as heretofore applied tend to become somewhat horny and thus become less active against mites. Yet these same compounds have been found highly effective under warmer conditions. It is, therefore, desired to so formulate them as to increase their activity under a wide range of climatic conditions. Of course, such formulations should not only be compatible with other common pesticidal formulations so as to permit their conjoint application, but also they must be relatively non-phytotoxic to the host plants.

The 1,1-bis(halophenyl)-2,2,2-trichloroethanols are miticidal agents, the preparation of which is described in U.S. Patents No. 2,812,280 and 2,812,362. The product, 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol is a well-known commercial miticide and there are various pesticidal compositions which utilize it as an active miticide.

In accordance with the present invention, emulsion concentrates and wettable powder formulations containing a 1,1-bis(halophenyl)-2,2,2-trichloroethanol as an active miticidal agent have been evolved which show excellent compatibility when admixed in a spray tank with other formulated pesticides, which promise favorable miticidal effectiveness under adverse climatic conditions, and which have acceptable phytotoxic properties.

The emulsion concentrates of this invention comprise 1,1-bis(halophenyl)-2,2,2-trichloroethanol dissolved in an alkyl oleate with the incorporation of emulsifying agent. The ratio of the 1,1-bis(halophenyl)-2,2,2-trichloroethanol to alkyl oleate may be varied from one part of such compound to four parts of the alkyl oleate to 1.25 parts to one part. Preferably, the ratios are from 1:2 to 1:1.

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Emulsifying agents are used in the concentration range of about 9 to about 20% by weight based on the emulsifiable concentrate and preferably 10% to 15%.

If desired, other pesticides may be incorporated. For example, dinitroalkylphenyl, especially the dinitro(2-methylheptyl)-phenyl, esters of crotonic, acrylic, methacrylic, β,β -dimethylacrylic, and 4-pentenoic acids which have been shown to have miticidal, insecticidal, and fungicidal properties may be advantageously added to these concentrates, and likewise such insecticidal agents as 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane, 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane, or 1,1-dichloro-2,2-bis(ethylphenyl)-ethane, phosphatic pesticides such as O,O-dimethyl S-(1,2-dicarbethoxyethyl) dithiophosphate, and 1-naphthyl N-methylcarbamate. It is often desirable to blend 1,1-bis(halophenyl)-2,2,2-trichloroethanol with pesticidal agents which kill mite predators and which, when used alone, thus cause a build-up of the mite population. In general from 5 to 25% of pesticidal agents of the above type may be added to an emulsion concentrate. The percentage depends in part on the solubility of the particular pesticidal agent being incorporated.

The wettable powder formulations of this invention are made by mixing an inert, finely-divided, solid carrier with the emulsion concentrate. There may be used from 5% to 25% by weight of 1,1-bis(halophenyl)-2,2,2-trichloroethanol in such compositions, this compound being dissolved in alkyl oleate together with emulsifiers. The amount of the emulsion concentrate added to the inert solid will vary with the capacity of each individual carrier or combination of carriers to hold the liquid and still maintain the product as a powder of loose texture.

The preferred 1,1-bis(halophenyl)-2,2,2-trichloroethanol used in this invention is 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethanol. It may be used in a pure form or as a technical grade containing isomers having bis(orthochlorophenyl) groups and the p, o'-dichloro-diphenyl groups as minor components. Also, the corresponding bromophenyl and fluorophenyl analogs may be used alone or admixed with 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol.

As the solvent for the preparation of the emulsion concentrates there is used methyl oleate, ethyl oleate, or mixtures of these two. One purpose of the solvent is to act as a plasticizer for the 1,1-bis(halophenyl)-2,2,2-trichloroethanol and thus keep the active ingredient in a fluid condition at low temperatures. It is also desirable to have the emulsion concentrates flowable after prolonged storage at ambient temperatures in cold weather. For these reasons the oleic acid ester or mixture of esters used must have a low setting point; i.e., the temperature range wherein a solid forms. This point will vary with purity of the oleates and should be no more than 60° F. (about 16° C.). There may be used relatively pure alkyl oleates or commercially available technical products.

As emulsifying agents there may be used surface active ethylene oxide adducts of alkyl mercaptans, long-chained carboxylic acids, higher alcohols, and alkylphenols wherein the ethylene oxide content of the resulting product is about 15 to 100 ether units, preferably 20 to 70 units. In general the alkyl mercaptans and higher alcohols should have 10 to 20 carbon atoms in their alkyl groups, while the acids should contain 12 to 24 carbon atoms in their carboxylic portion, which may be a straight or branched chain or a cycle, as in abietic acid. Typical of these are t-tetradecylthiopolyethoxyethanol, tall-oil-acid polyethoxyethanol, dodecyloxy polyethoxyethanol, and alkylphenoxy polyethoxyethanol, wherein the alkyl group or groups contain 8 to 12 carbon atoms and the main group occurs preferably in the para position but that position is immaterial. There may also be used ethylene oxide adducts

of partially esterified sorbitols and similar polyhydric alcohols, the esters being formed with such long-chained acids as oleic or lauric acids.

Also, there are used surface active, oil-soluble calcium and magnesium salts of alkylarenesulfonic acids wherein the alkyl group or groups contain from 8 to 18 carbon atoms in admixtures with the above described ethylene oxide adducts. The preferred sulfonates are salts of alkylbenzenesulfonic acid, such as calcium p-t-dodecylbenzenesulfonate. There may also be used similar alkyl naphthalenesulfonic acid salts, such as calcium octyl-naphthalenesulfonates.

The ratio of weights of the ethylene oxide adduct to the sulfonate may vary from about 3:1 to about 1:1.

To prepare the wettable powders from the emulsion concentrates, a variety of finely dispersed solid carriers may be used. It is necessary to use inert solids to avoid a carrier that is strongly basic since basic agents tend to decompose the 1,1 - bis-(halophenyl)-2,2,2-trichloroethanols. Examples of inert finely divided carriers useful for the preparation of these wettable powders are the finely particled clays such as fuller's earth and kaolins, silica, diatomaceous earth, and alkaline earth silicates, particularly those silicates which have been carbonated to neutralize any basic impurities.

It is often desirable to incorporate dispersing agents into the wettable powders. Typical of these are the salts of polymers formed from maleic anhydride and olefinically unsaturated hydrocarbons such as styrene, alkylstyrenes, or diisobutylene. When ammonia or some amines are used to form salts, some amide or imide formation also occurs. The amount of the added dispersing agent is desirably 1% to 10% of the weight of the powder to which it is added.

Typical formulations and products of this invention are illustrated by the following examples. Parts are by weight unless otherwise designated.

Example 1

(a) There are mixed 50 parts of commercial 1,1-bis-(chlorophenyl)-2,2,2-trichloroethanol and 40 parts of commercial methyl oleate having a set point of about -16° C. to give a homogeneous solution. Thereto are added 5 parts of p-diisobutylphenoxypolyethoxyethanol containing about 30 ether groups and 5 parts of calcium dodecylbenzenesulfonate. The mixture is stirred and warmed until homogeneous.

The resulting emulsion concentrate may be diluted with water to provide an efficient spray for protection against mites. It is compatible with wettable powders containing fungicides such as wettable sulfur, ferbam, zineb, and maneb, with DDT, and with phosphatics.

(b) There are taken 50 parts of the above emulsion concentrate and 50 parts of finely divided hydrated silica. These are milled until a uniform wettable powder results. This powder is compatible with preparations of other pesticides.

Example 2

(a) In the same way there are mixed 40 parts of relatively pure 1,1 - bis(p - chlorophenyl)-2,2,2-trichloroethanol, 40 parts of methyl oleate having a set point of $+16^{\circ}$ C., and 20 parts of an emulsifier containing 60% by weight of nonylphenoxypolyethoxyethanol having about 20 ether groups and 40% of calcium dodecylmethylbenzenesulfonate. The product is useful and effective as an emulsion concentrate and can be diluted with water for spraying. It is compatible with the usual preparations of other pesticides.

(b) There are mixed 40 parts of the above emulsion concentrate, 50 parts of hydrated silica, and 10 parts of fuller's earth. The mixture is then blended with five parts of the sodium salt formed from the copolymer from equal moles of maleic anhydride and diisobutylene. The resulting wettable powder is readily dispersed in water,

it has good suspendibility in waters of varying hardness, and its application properties to foliage are entirely acceptable from its aqueous sprays.

In place of the above sodium salt used as a dispersant there may be used other common dispersing agents such as sodium or calcium lignosulfonates. These serve to provide good suspendibility, but it has been observed that compositions utilizing these sulfonates tend to deteriorate on extended storage. This improvement in suspendability in recently prepared mixtures is also observed when the dispersing agent is a salt of a condensed formaldehyde-naphthalene sulfonate such as sodium formaldehyde-naphthalene sulfonate as sold under the trade names of Daxad or Tamol.

Example 3

(a) There are mixed 20 parts of technical 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol, 65 parts of methyl oleate (set point about 0° C.), and 15 parts of an emulsifier from 10 parts of long-chained fatty acid-ethylene oxide adduct, having about 50 ether groups per molecule and 5 parts of calcium tetradecylbenzenesulfonate. The resulting emulsion concentrate is stable on storage and is readily dispersed in even hard water to give effective aqueous sprays.

(b) There are mixed 50 parts of the above emulsion concentrate and 50 parts of finely divided sodium silico-aluminate (Zeolex 23) to form a useful wettable powder. The initial suspendibility is very good for this product, but storage characteristics are improved by blending therewith 3 to 10% of the ammonium salt of the copolymer from maleic anhydride, diisobutylene, and styrene.

The above formulation, repeated with substitution of an equal weight of ethyl oleate for the methyl oleate, provides another efficient emulsion concentrate which, when blended with finely divided carriers, gives useful wettable powders. There may likewise be used mixtures of methyl and ethyl oleates with like outcomes.

The emulsion concentrates of this invention can be readily formulated so as to be acceptably low in phytotoxicity on plants, even on flush citrus growth. This is also true of properly formulated wettable powders. Since the alkyl oleates are very high boiling and have high flash points, they can be used in grinding machinery without hazard. Because of the low volatility of the alkyl oleates the active agents remain in a fluid and active state. Most important of all, however, is the unusual degree of compatibility of compositions of this invention with many common formulations of other pesticides.

We claim:

1. A miticidal composition comprising as an active miticidal agent a 1,1-bis(halophenyl)-2,2,2-trichloroethanol dissolved in an alkyl oleate in which the alkyl group contains one to two carbon atoms together with emulsifying agents consisting of a surface active ethylene oxide adduct having 15 to 100 ether units and a surface active oil-soluble alkylarenesulfonate, the ratio of the ethylene oxide adduct to the alkylarenesulfonate varying from about 3:1 to about 1:1 by weight.

2. A miticidal composition comprising as an active miticidal agent 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol and emulsifying agents dissolved in an alkyl oleate in which the alkyl group contains one to two carbon atoms, the ratio of said 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol to said alkyl oleate being from 1:4 to 1.25:1 and the emulsifying agents consisting of a surface active ethylene oxide adduct having 15 to 100 ether units and a surface active oil-soluble alkylarenesulfonate, the ratio of the ethylene oxide adduct to the alkylarenesulfonate varying from about 3:1 to about 1:1 by weight.

3. A miticidal composition in the form of a wettable powder comprising a finely divided inert solid carrying a solution of 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol and emulsifying agents in an alkyl oleate in which the

alkyl group contains one to two carbon atoms, the ratio of said 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol to said alkyl oleate being from 1:4 to 1.25:1 and the emulsifying agents consisting of a surface active ethylene oxide adduct having 15 to 100 ether units and a surface active oil-soluble alkylarenesulfonate, the ratio of the ethylene oxide adduct to the alkylarenesulfonate varying from about 3:1 to about 1:1 by weight.

4. A miticidal composition comprising a solution of 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol and emulsifying agents in at least one alkyl oleate in which the alkyl group contains one to two carbon atoms, the ratio of said 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol to said alkyl oleate being from 1:4 to 1.25:1 and the emulsifying agents consisting of a surface active ethylene oxide adduct having 15 to 100 ether units and a surface active, oil-soluble alkylbenzenesulfonate wherein the alkyl group contains from 8 to 18 carbon atoms, the ratio of the ethylene oxide adduct to the alkylbenzenesulfonate varying from about 3:1 to about 1:1 by weight, the said emulsifying agents providing about 9% to 20% of the weight of the solution.

5. A miticidal composition in the form of a wettable powder comprising a finely divided inert solid carrying a solution of 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol and emulsifying agents in an alkyl oleate in which the alkyl group contains one to two carbon atoms, the ratio of said 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol to said alkyl oleate being from 1:4 to 1.25:1 and the emulsifying agents consisting of a surface active ethylene oxide adduct having 15 to 100 ether units and a surface active, oil-soluble alkylbenzenesulfonate wherein the alkyl substituent contains from 8 to 18 carbon atoms, the ratio of the ethylene oxide adduct to the alkylbenzenesulfonate varying from about 3:1 to about 1:1 by weight, the said emulsifying agents providing about 9% to 20% of the weight of the solution, and the percentage of the said 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol being from 5% to 25% of the weight of the composition.

6. A composition according to claim 5 in which there is added to the wettable powder 1% to 10% by weight of a dispersing agent.

7. A composition according to claim 6 in which the dispersing agent is a salt of a polymer of maleic anhydride and diisobutylene.

8. A miticidal composition in the form of a wettable powder comprising a finely divided hydrated silica carrying a solution of 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol and emulsifying agents in methyl oleate, the ratio of said 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol to said methyl oleate being from 1:4 to 1.25:1 and the emulsifying agents consisting of an alkylphenoxypolyethoxyethanol having 20 to 70 ether units and containing 8 to 12 carbon atoms in its alkyl substituent and a surface active, oil-soluble calcium alkylbenzenesulfonate wherein the alkyl substituent contains from 8 to 18 carbon atoms, the ratio of the alkylphenoxypolyethoxyethanol to the calcium alkylbenzenesulfonate being about 3:1 to about 1:1 by weight, the said emulsifying agents providing about 9% to 20% of the weight of the solution, and the percentage of the said 1,1-bis(chlorophenyl)-2,2,2-

trichloroethanol being about 5% to 25% of the weight of the composition.

9. A composition according to claim 8 in which the alkylphenoxypolyethoxyethanol is diisobutylphenoxypolyethoxyethanol.

10. A composition according to claim 8 in which the calcium alkylbenzenesulfonate is calcium dodecylbenzenesulfonate.

11. A miticidal composition comprising a solution of 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol and emulsifying agents in methyl oleate, the ratio of said 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol to methyl oleate being from 1:2 to 1:1 and the emulsifying agents consisting of an alkylphenoxypolyethoxyethanol having 20 to 70 ether units and containing 8 to 12 carbon atoms in its alkyl substituent and a surface active, oil-soluble calcium alkylbenzenesulfonate wherein the alkyl substituent contains from 8 to 18 carbon atoms, the ratio of the alkylphenoxypolyethoxyethanol to the calcium alkylbenzenesulfonate being about 3:1 to about 1:1 by weight, the said emulsifying agent providing about 9% to 20% of the weight of the solution.

12. A composition according to claim 11 in which the alkylphenoxypolyethoxyethanol is diisobutylphenoxypolyethoxyethanol.

13. A composition according to claim 11 in which the calcium alkylbenzenesulfonate is calcium dodecylbenzenesulfonate.

14. A miticidal composition comprising a solution of about 50% by weight of 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol and 10% by weight of emulsifying agents in methyl oleate, the emulsifying agents consisting of p-diisobutylphenoxypolyethoxyethanol containing about 30 ether groups and calcium dodecylbenzenesulfonate in about equal weights.

15. A miticidal composition comprising about 50% by weight of a finely divided hydrated silica carrying about an equal weight of a solution of about 50 parts by weight of 1,1-bis(chlorophenyl)-2,2,2-trichloroethanol and 10 parts by weight of emulsifying agents dissolved in 40 parts by weight of methyl oleate, the emulsifying agents consisting of p-diisobutylphenoxypolyethoxyethanol containing about 30 ether groups and calcium dodecylbenzenesulfonate in about equal weights.

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