Patented Oct. 30, 1951

2,572,946

UNITED STATES PATENT OFFICE

2,572,946

COMPOSITION COMPRISING 2-ALIPHATIC-3-HYDROXY-1,4 NAPTHOQUINONE AND METHOD FOR CONTROLLING MITES AND APHIDS

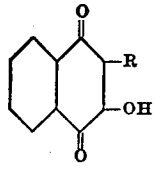
Marvin Paulshock, Wilmington, Del., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application November 19, 1949, Serial No. 128,491

5 Claims. (Cl. 167—30)

1

This invention relates to insecticidal compositions and more especially to compositions adapted for the control of mites and aphids. The compositions of the invention employ as an essential active ingredient a compound represented by the formula



where R is a radical, containing from 6 thru 15 carbon atoms, selected from the group consisting of alkyl, cyclohexyl, and cyclohexylalkyl; and the salts of said compounds. These compounds will be referred to hereafter more briefly as 2-aliphatic-3-hydroxy-1,4-naphthoquinones, it being understood that the term aliphatic so used is intended to include not only alkyl radicals, but also cyclohexyl, and cyclohexylalkyl radicals.

It is an object of this invention to provide compositions and methods for the control of insects and particularly for the control of mites and aphids. It is a further object to provide solutions, water-dispersible liquids, dusts and water-dispersible powders which are effective in killing mites and aphids in all stages of their development. A still further object is to provide compositions which may be used for protecting growing plants against mite and aphid infestation without injuring the plants. Still other objects will become apparent hereinafter.

The foregoing and other objects of the invention are attained by means of compositions containing a 2-aliphatic-3-hydroxy-1,4-naphthoquinone responding to the formula and definition set out above in admixture with an adjuvant having dispersing properties. The compositions of the invention are characterized by the admixture of a dispersing agent with a 2-aliphatic-3-hydroxy-1,4-naphthoquinone and these compositions may also be formulated with other appropriate adjuvants to give mite killing and aphid killing compositions in the form of solutions, water-dispersible liquids, dusts and water-dispersible powders.

The 2-aliphatic-3-hydroxy - 1,4-naphthoquinones are prepared by alkylation of lawsone, 2-hydroxy-1,4-naphthoquinone, with a diacyl peroxide. The compounds are water insoluble yellow to orange colored solids having melting points in the range of about 50–150° C. The salts of

2

the compounds are readily prepared by reaction, for example with an amine or a metal hydroxide. The salts are slightly water soluble red colored solids which decompose on heating.

Illustrative of the 2-aliphatic-3-hydroxy-1,4-naphthoquinones employed in the compositions of the invention are compounds represented by the formula given above in which: R is n-alkyl, such as hexyl, octyl, nonyl, decyl, hendecyl, dodecyl, tridecyl, tetradecyl, pentadecyl; R is branched chain such as 2-methyloctyl, isononyl, 2,4-dimethylpentyl, and 1-isopropyl-2-methylbutyl; R is cyclohexyl; R is cyclohexylalkyl such as cyclohexylmethyl, 3-cyclohexylpropyl, 4-cyclohexylbutyl, 6-cyclohexylhexyl, 8-cyclohexyloctyl, 9-cyclohexylnonyl; and the salts of any of the foregoing compounds, such as the sodium or other alkaline earth or alkaline metal salts and dimethylamine or similar amine salts.

The preferred 2-aliphatic-3-hydroxy-1,4-naphthoquinones employed in the compositions of the invention are those in which R is normal alkyl and still more preferably those in which R is n-alkyl containing from 11 thru 14 carbon atoms specifically the n-hendecyl-, n-dodecyl-, n-tridecyl-, and n-tetradecyl-3-hydroxy-1,4-naphthoquinones.

In preparing the compositions of the invention, a 2-aliphatic-3-hydroxy-1,4-naphthoquinone is admixed with a surface active agent of the type used to impart dispersibility of an organic liquid composition or a powder in water. Such agents will be referred to herein as dispersing agents since they cause the compositions of the invention, whether in liquid or in powdered form, to be easily dispersed in water to give aqueous spray compositions. Such agents when used in admixture with an organic liquid composition are sometimes also referred to in the art as emulsifying agents since the dispersion of the organic liquid in water which they promote is an emulsion.

Where a water-dispersible organic liquid composition containing a 2-aliphatic-3-hydroxy-1,4-naphthoquinone is desired, the dispersing agent used is preferably one that is soluble in the organic liquid used as solvent for the insecticidal agent. Typical of such oil-soluble dispersing, or emulsifying, agents are the amine salts of oleic acid, the sulfonated animal and vegetable oils such as sulfonated fish and castor oils, sulfonated petroleum oils, glycerol monostearate, sorbitan tristearate, diglycol oleate, diethylene glycol laurate, pentaerythritol monostearate, phthalic glycerol alkyd resins, and polyethylene oxides.

In the preparation of water-dispersible pow-

dered compositions of the invention, the oil-soluble dispersing agents of the type illustrated above may be used and other dispersing agents which are not generally thought of as oil-soluble may also be employed. Examples of the latter are the calcium or sodium salts of lignin sulfonic acid such as goulac, polyvinyl alcohols, and the sodium salts of sulfonated condensation products of naphthalene and formaldehyde.

Other dispersing agents are listed in detail in U. S. Department of Agriculture Bulletin E-607 and in an article by McCutcheon in Chemical Industries, November 1947, page 811, entitled "Synthetic Detergents."

The amount of dispersing agent used in the compositions of the invention will vary with the dispersing properties of the particular adjuvant used and will be varied too with the particular use for which the composition is intended. Generally the dispersing agent will not comprise more than about 10% by weight of the composition and with the better adjuvant materials, the percentage will be 5% or less.

The compositions of the inventions consisting of a 2-aliphatic-3-hydroxy-1,4-naphthoquinone in admixture with a dispersing agent may be used as such in the preparation of aqueous spray compositions or, alternatively, they may be diluted with solvents to give solutions and water-dispersible liquids, or they may be diluted with finely-divided inert powders to give dusts and water-dispersible powders.

It is preferred to prepare the compositions of the invention in the form of concentrates, that is, solutions or dusts containing the toxicant in high concentration. These concentrates are then dispersed or diluted before actual application. Such dispersion or dilution is obtained by mixing the compositions with additional amounts of diluent, solvents or dusts, or more preferably by dispersing the compositions in water to give aqueous emulsions or suspensions which are readily applied by means of the conventional insecticidal spray equipment.

In preparing the water-dispersible dust compositions of the invention, the finely-divided inert powder used as a diluent is preferably selected from the class consisting of talcs, pyrophyllite, natural clays, and diatomaceous earths. Other powdered inert diluents which may be used in dust compositions include powders such as calcium phosphate, calcium carbonate, magnesium carbonate, sulfur, lime, and flours such as walnut shell, wheat, redwood, soya bean, and cottonseed.

Various solvents may be used if it is desired to prepare solutions containing a 2-aliphatic-3-hydroxy-1,4-naphthoquinone and a dispersing agent. Typical solvents are kerosene, trichloroethylene, tetrachloroethylene, alkylated naphthalene, xylene, toluene, cyclohexanone, and acetone. One should bet careful, however, in the selection of a solvent diluent if it is desired to apply a solution to growing crops since many of the common solvents tend to damage plants.

The concentration of the active ingredient in the concentrates may be varied widely. For example, compositions in the form of dusts or water-dispersible powders can be prepared containing from 1 to about 65% by weight of the active ingredient. The maximum concentrations obtained in the preparation of solutions will, of course, vary according to the solubility of the active toxicant in the particular solvent selected.

In actual application to vegetation or agricultural crops, the concentrates are diluted and the compositions applied in the form of a dust or an aqueous spray containing preferably from about 0.001 to 0.1% by weight of the 2-aliphatic-3-hydroxy-1,4-naphthoquinone.

In applying the compositions of the invention for the control of aphids and other insects and for the control of mites, the compositions are applied directly on the area or locus which is to be protected from the pest infestation in amount sufficient to exert an insecticidal or miticidal action. It is not necessary that the composition be applied directly to the pests.

While the compositions of the invention include as an essential active ingredient a 2-aliphatic-3-hydroxy-1,4-naphthoquinone in admixture with a dispersing agent, they may also include insect toxicants, bactericides, and fungicides such as those disclosed in U. S. Patent 2,426,417.

The invention is illustrated further by reference to the following examples:

Example I

2-cyclohexyl-3-hydroxy-1,4 - naphthoquinone (yellow needles, M. P. 135° C.) is mixed with the dispersing agent glycerol monostearate in proportions to give 95% by weight of the toxicant and 5% by weight of the dispersing agent.

The above concentrate is readily dispersible in water to provide aqueous spray compositions. A spray composition adapted for application to apple trees for the protection of the trees against infestation by mites and aphids is obtained by dispersing the composition of this example in water to give an aqueous suspension containing from 0.001 to 0.01% by weight of 2-cyclohexyl-3-hydroxy-1,4-naphthoquinone.

Example II

The following is an example of a dust and water-dispersible powder composition of the invention. It is prepared by mixing the ingredients tabulated below to obtain a finely-divided solid.

10% 2 - n - dodecyl-3-hydroxy-1,4-naphthoquinone (yellow powder, M. P. 93.8–94.6° C.)
85% pyrophyllite (average particle size less than 40 microns)
5% pentaerythritol monostearate

The composition of this example is applied as a dust or more preferably it is dispersed in water to form an aqueous suspension for application as a spray for the control of mites and aphids.

Example III

Following is a solution or water-dispersible liquid composition of the invention:

1% 2-(9-cyclohexylnonyl)-3-hydroxy-1,4-naphthoquinone (yellow powder M. P. 97–98° C.)
96% alkylated naphthalene
3% diethyl cyclohexylamine dodecyl sulfate

The composition of this example is readily dispersible in water. A spray composition well suited for the control of mites is obtained by dispersing a quart of the above formulation in 100 gallons of water.

Example IV

Powdered 2 - tridecyl-3-hydroxy-1,4-naphthoquinone, sodium salt is thoroughly mixed with finely ground fuller's earth and the dispersing agent goulac in proportions to give 50% by weight of the insecticidal agent, 45% by weight fuller's earth, and 5% by weight goulac.

The composition of this example is a concentrate adapted for dispersion in water to give sus-

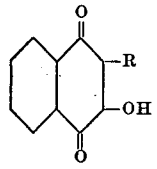
pensions suitable for application by means of conventional agricultural spray equipment.

Example V

A mixture of 5 parts by weight of the dimethylamine salt of 2-methyloctyl-3-hydroxy-1,4-naphthoquinone, 90 parts by weight of talc, and 5 parts by weight of diglycol oleate is pulverized and mixed to give a composition adapted for application as a dust or in the form of an aqueous suspension for the control of mites and aphids.

I claim:

1. A composition adapted for the control of mites and aphids which comprises as an essential active ingredient in admixture with a surface active agent in amount effective for imparting water dispersability to the composition a 2-aliphatic-3-hydroxy-1,4-naphthoquinone represented by the formula



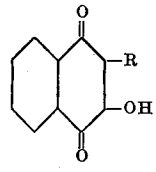
where R is a radical, containing from 6 thru 15 carbon atoms, selected from the group consisting of alkyl, cyclohexyl, and cyclohexylalkyl; and the salts thereof.

2. A composition for the control of mites and aphids which comprises as an essential active ingredient in admixture with a surface active agent in amount effective for imparting water dispersability to the composition a 2-n-alkyl-3-hydroxy-1,4-naphthoquinone, in which the n-alkyl radical contains 6 thru 15 carbon atoms.

3. A composition adapted for the control of mites and aphids which comprises as an essential active ingredient in admixture with a surface active agent in amount effective for imparting water dispersability to the composition a 2-n-alkyl-3-hydroxy-1,4-naphthoquinone, in which the n-alkyl radical contains 11 thru 14 carbon atoms.

4. A composition adapted for the control of mites and aphids comprising 2-n-dodecyl-3-hydroxy-1,4-naphthoquinone as an essential active ingredient in admixture with a surface active agent in amount effective for imparting water dispersability to the composition.

5. The method of protecting plants from infestation by mites and aphids which comprises applying to the plants a composition containing as an essential active ingredient a 2-aliphatic-3-hydroxy-1,4-naphthoquinone represented by the formula



where R is a radical, containing from 6 thru 15 carbon atoms, selected from the group consisting of alkyl, cyclohexyl, and cyclohexylalkyl; and the salts thereof.

MARVIN PAULSHOCK.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,752,293	Brodersen et al.	Apr. 1, 1930
2,348,976	Hyman	May 16, 1944
2,398,418	Fieser	Apr. 16, 1946
2,435,500	Ladd	Feb. 3, 1948

OTHER REFERENCES

Anfinsen et al.: Chemical Abstracts, vol. 41, page 7539f (1947).