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INSECTICIDAL SPRAY MATERIALS

William S. Calcott, Pennsgrove, N. J., and Wendell H. Tisdale and Albert L. Flenner, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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This invention relates to insecticidal spray materials and more particularly to new and improved insecticidal compounds.

Many insecticidal compounds have been dissolved or suspended in water and oil-in-water emulsions and similar liquid media and the resulting solutions, suspensions and emulsions have been employed as insecticidal sprays. These various spray materials have met with varying degrees of success but none have proved to be entirely satisfactory for our purposes.

An object of the present invention is to provide new insecticidal spray materials. A further object is to provide insecticidal spray materials comprising aqueous liquids having incorporated therein acid salts of organic lead compounds as the main insecticidal ingredients. Another object is to provide a method for controlling insects. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

These objects may be accomplished in accordance with our invention which comprises incorporating, in aqueous liquids to be employed as insecticidal spray materials, acid salts of organic lead compounds having the formula:

$$RmPbXn$$

wherein R represents an unsubstituted hydrocarbon radical, m represents at least 2, n represents at least 1, and m plus n equals 4. The most effective compounds of this type are those in which m represents 3. Therefore the compounds which we prefer may be more specifically represented by the formula:

$$R_3PbX$$

wherein R represents an unsubstituted hydrocarbon radical and X represents an acid radical.

The term "unsubstituted hydrocarbon radical" as employed herein includes radicals such as methyl, ethyl, propyl, butyl, phenyl, tolyl, naphthyl and benzyl radicals. In other words, "unsubstituted hydrocarbon radical" means a radical consisting solely of carbon and hydrogen.

The term "acid" as employed herein is to be understood to have its commonly accepted meaning and not to include compounds such as phenol which have acidic properties under some conditions and are sometimes termed acids.

The most effective compounds of our claims are the compounds in which X in the formula

$$R_3PbX$$

represents a thiocyanic acid radical. Of these, triethyl lead thiocyanate and triphenyl lead thiocyanate are preferred. Among the other compounds which we have found to be particularly satisfactory for our purpose are triethyl lead oleate, triphenyl lead oleate, triethyl lead stearate, triethyl lead resinate, triethyl lead nitrate, triethyl lead formate, triethyl lead aceto thiocyanate, triethyl lead dithiocarbamate, triethyl lead thioglycolate, triethyl lead cyanide, and triethyl lead thiosulphate.

In order to more clearly illustrate our invention and the preferred modes of carrying the same into effect and the advantageous results to be obtained thereby, the following examples are given:

Example 1

Triethyl lead oleate was dissolved in diethyl ammonium oleate to make a 20% solution of triethyl lead oleate. This solution was employed at the rate of 0.10% in soft water to spray chrysanthemum plants infested with black aphis. More than 95% of the aphis were killed within 24 hours and no injury was caused to the plants.

Example 2

When triphenyl lead oleate was substituted for the triethyl lead of Example 1, the composition and method being otherwise the same, essentially the same results were obtained.

Example 3

An oil emulsion containing 3% of triethyl lead oleate was diluted with water to form an emulsion containing one part of the oil emulsion to 200 parts of water. This diluted emulsion was sprayed on a viburnum plant infested with brown aphids. Approximately 95% of the aphids were killed and no injury was caused to the plant.

Example 4

One part of an oil emulsion, containing 5% diethyl lead dioleate, was diluted with 150 parts of water and sprayed on chrysanthemum plants

infested with black aphis. This killed approximately 25% of the aphis and caused no injury to the plant.

Example 5

One part of diethyl ammonium oleate, containing 20% triethyl lead stearate, was diluted with 1000 parts of water. Upon being sprayed on chrysanthemum plants, this material killed over 95% of the black aphids thereon but slightly burned the plants.

Example 6

One part of a solution of 20% triethyl lead resinate in diethyl ammonium oleate was diluted with 1000 parts of water. This diluted solution killed approximately 96% of black chrysanthemum aphis and caused no injury to the plants.

Example 7

One part of a mixture of the sodium salt of sulfonated fish oil and the triethyl lead salt of sulfonated fish oil was diluted with 500 parts of water. This material contained the equivalent of one part of tetraethyl lead in 5000 parts of material. When this material was sprayed on aphid infested chrysanthemum plants, more than 95% of the aphids were killed without causing any injury to the plants.

Example 8

One part of triethyl lead nitrate was diluted with 4000 parts of water containing 0.1% of diethyl ammonium oleate as a wetting agent. Upon spraying chrysanthemum plants with this diluted material, 97% of the black aphids were killed.

Example 9

One part of diethyl ammonium oleate, containing 20% triethyl lead thiocyanate in solution, was diluted with 2000 parts of soft water. This material killed more than 97% of the chrysanthemum aphids upon being sprayed thereon.

Example 10

One part of triethyl lead formate was diluted with 5000 parts of water containing 0.1% of diethyl ammonium oleate employed as a spreading agent. This material killed approximately 96% of black aphis of chrysanthemum.

Example 11

Triethyl lead aceto thiocyanate was dissolved in diethyl ammonium oleate and this solution was diluted with water; the proportions being such that, in the final material, there was one part of the lead compound for every 15,000 parts of water and one part of amine soap to every 1000 parts of water. When this material was employed as a spray, it killed approximately 90% of black chrysanthemum aphis in 24 hours.

Example 12

One part of triethyl lead dithiocarbamate was suspended in 5000 parts of water, employing 10 parts of diethyl ammonium oleate as an emulsifier and spreading agent. This spray material killed more than 98% of black chrysanthemum aphis in 24 hours.

Example 13

One part of triethyl lead thioglycolate was diluted with 5000 parts of water containing 0.1% of sulphonated cod oil as a spreader. This material killed approximately 95% of black chrysanthemum aphis in 24 hours.

Example 14

One part of triethyl lead cyanide was diluted with 5000 parts of water containing 0.1% of diethyl ammonium oleate as a spreader. This material killed more than 90% of green potato aphis but slightly burned the foliage.

Example 15

One part of triethyl lead thiosulfate was diluted with 4000 parts of water containing 0.1% of diethyl ammonium oleate as a spreader. This material, on being sprayed on potatoes infested with green aphids, killed more than 90% of the aphids.

Example 16

One part of an oil emulsion containing 1.5% triethyl lead oleate was diluted with 60 parts of water and sprayed on lemons infested with red scale. More than 90% of the adult scale insects were killed.

Example 17

One part of a miscible oil containing 2.5% of triethyl lead oleate when diluted with 50 parts of water and sprayed on the pupae of the codling moth, killed approximately 80% of the pupae.

While the above examples illustrate the results to be obtained with some of our compounds it is to be understood that such examples are illustrative only and many other examples could be given without, however, serving any useful purpose, as the above examples represent the results to be obtained with the various members of our class. Accordingly, other compounds within our class which may be employed effectively for our purpose are more generally indicated hereinafter.

It will be found that results similar to those shown in the examples will be obtained if other hydrocarbon radicals such as methyl, propyl, butyl, tolyl, benzyl, naphthyl and the like are substituted for the ethyl and phenyl radicals. Also, compounds, in which m and n of our formula $RmPbXn$ represent the integer 2, will be found to be effective. Furthermore, X in our formula may represent other organic or inorganic acid radicals, than oleic, stearic, resinic, sulfonated fish oil, nitric, thiocyanic, formic, aceto thiocyanic, dithiocarbamic, thioglycolic, cyanic and thiosulfuric. Some of these other acid radicals are those of palmitic, butyric, acetic, lactic, tannic, abietic, arsenic, fluosilicic, other dithiocarbamic acids, sulfuric, hydrochloric, hydrobromic and like acids. Other radicals may be introduced into the acid part of the compounds to render the compounds more stable and less volatile. Such radicals may be represented by the acyl radicals such as acetyl as in aceto cyanic acid. The trihydrocarbon lead salts of these various acids will, in the majority of cases, be found to be materially more effective than other salts of these acids which have heretofore been employed for this purpose. This characteristic of our compound is particularly apparent in the triethyl and triphenyl lead thiocyanates and dithiocarbamates which are materially more effective than other thiocyanates and dithiocarbamates heretofore employed.

The organic lead sulfonates have also been found to have insecticidal properties and also

are generally good dispersing and wetting agents. For example, the triethyl lead sulfonates and triphenyl lead sulfonates, prepared from sulfonated oils such as animal, vegetable, and mineral oils, have contact insecticidal properties and are good dispersing and wetting agents. Likewise, the triethyl lead or triphenyl lead and related salts of sulfonated compounds, such as lauryl sulfonate, sulfonated glycerol abietate, isopropyl sulfonic acid, isopropyl naphthalene sulfonic acid, sulfonated higher alcohols comprising mixed fractions of straight and side chain types, and other similar sulfonated compounds which have been employed as detergents or wetting agents, combine the properties of dispersing and wetting agents with effective insecticidal properties. These organic lead compounds of sulfonated oils and the like are generally less effective insecticides than the other compounds of our invention but have the advantage of being complete within themselves and may be readily dispersed in water without the addition of other wetting agents. Their solutions will readily spread and wet the leaves and the insects.

Other specific compounds within our class, which may be mentioned, are triethyl lead chloride, triethyl lead thiocyano oleate, triethyl lead sulfide, diphenyl lead dibromide, dimethyl lead dichloride, diethyl lead sulfate, dicyclohexyl lead dichloride and triphenyl lead chloride.

Some of our compounds are readily soluble in water and may be employed in a straight water solution. Other compounds of our invention are soluble in oil. These compounds are particularly adapted for use in oil-in-water emulsions. Other compounds of our invention are relatively insoluble in water and oil but are soluble in amine soaps which are good dispersing and wetting agents. Such compounds may be first dissolved in the amine soaps and such solutions may be incorporated in water or in oil-in-water emulsions. Other compounds of our invention are insoluble in water, oil and the amine soaps. These last compounds may be suspended in water or oil-in-water emulsions in finely divided form or may be dissolved in other solvents and then incorporated in the water or oil emulsions and the like, provided that care is taken to employ a solvent which is non-injurious to the plant to which the spray is to be applied.

The relatively insoluble compounds will generally be found to fall within the class represented by the formula RmPbXn, wherein both m and n represent the integer 2. The compounds falling within the formula R_3PbX will generally be found to be the most effective and the most soluble and will generally be preferred.

In general, the compounds of our invention are old and well known chemical compounds and the methods of making them are also well known and are described in the literature.

While we have disclosed specific embodiments of our invention, it will be readily apparent to those skilled in the art that many variations and modifications may be made therein and the proportions employed without departing from the spirit of our invention. Accordingly, the scope of our invention is to be limited solely by the appended claims, construed as broadly as is permissible in view of the prior art.

We claim:

1. An insecticidal spray material comprising an aqueous liquid having incorporated therein a compound of the type:

RmPbXn

wherein R represents an unsubstituted hydrocarbon radical, X represents an acid radical, m represents at least 2, n represents at least 1, and m plus n equals 4.

2. An insecticidal spray material comprising an aqueous liquid having incorporated therein a compound of the type

R_3PbX

wherein R represents an unsubstituted hydrocarbon radical and X represents an acid radical.

3. An insecticidal spray material comprising water having incorporated therein an amine soap and a compound of the type:

RmPbXn

wherein R represents an unsubstituted hydrocarbon radical, X represents an acid radical, m represents at least 2, n represents at least 1, and m plus n equals 4.

4. An insecticidal spray material comprising an oil in water emulsion having incorporated therein a compound of the type:

RmPbXn

wherein R represents an unsubstituted hydrocarbon radical, X represents an acid radical, m represents at least 2, n represents at least 1, and m plus n equals 4.

5. An insecticidal spray material comprising an aqueous liquid having incorporated therein a compound of the type:

RmPbXn

wherein R represents an unsubstituted hydrocarbon radical, X represents an oleic acid radical, m represents at least 2, n represents at least 1, and m plus n equals 4.

6. An insecticidal spray material comprising an aqueous liquid having incorporated therein a compound of the type:

R_3PbX

wherein R represents an unsubstituted hydrocarbon radical and X represents an oleic acid radical.

7. The method of exterminating insects which comprises spraying the insects with an aqueous liquid having incorporated therein a compound of the type:

RmPbXn

wherein R represents an unsubstituted hydrocarbon radical, X represents an acid radical, m represents at least 2, n represents at least 1, and m plus n equals 4.

8. The method of exterminating insects which comprises spraying the insects with an aqueous liquid having incorporated therein a compound of the type:

R_3PbX

wherein R represents an unsubstituted hydrocarbon radical and X represents an acid radical.

WILLIAM S. CALCOTT.
WENDELL H. TISDALE.
ALBERT L. FLENNER.