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INSECTICIDAL AEROSOL COMPOSITIONS COMPRISING A 1,1,1-TRICHLORO-2,2-BIS(ETHOXY METHYL PHENYL) ETHANE IN A CHLORO-FLUOROMETHANE

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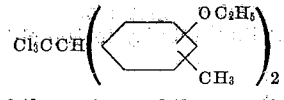
5 Claims. (Cl. 167—30)

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This invention relates to new and useful improvements in insecticidal compositions, more particularly it relates to an improved insecticide ideally adapted for aerosol dispersion.

Compounds of DDT type (1,1,1 tri-chloro-2,2-di (4-chloro-phenyl) ethane) are known to possess substantial insecticidal activity. These compounds have certain disadvantages, e. g., their knock-down strength is not very great, and consequently aerosol formulations of necessity usually include additional knock-down ingredients. In addition, DDT is only slightly soluble in aliphatic solvents so that auxiliary solvents, usually aromatic in character, often have to be employed. These latter type solvents have unpleasant odors, and hence are undesirable constituents of aerosol formulations.

It has now been found that aerosol insecticidal compositions containing as the active ingredient the reaction product of the condensation reaction between chloral hydrate and o-ethoxy toluene are ideally adapted to overcome the beforementioned difficulties. The active product of this invention is represented by the following formula, where either the ethoxy or methyl group is in a position para to the $CHCCl_3$ linkage and the group not in the para position is in an ortho position to the group in the para position:



Because of the nature of the reaction when the ethoxy group tends to occupy the position para to the $CHCCl_3$ linkage the methyl group of necessity assumes the meta position with respect to the tri-chloroethyl group, and retains its ortho position with respect to the ethoxy group. A similar analogy applies when the methyl substituent occupies the para position on the benzene ring. The active ingredients of this invention are thus a mixture of isomers which have in all cases an additional substituent on the benzene ring in addition to the substituent in the 4 or para position. The active ingredients of this invention are thus best characterized as the reaction product of the condensation reaction between chloral hydrate and o-ethoxy toluene.

The product of this invention is more soluble than DDT in aliphatic hydrocarbons so that odorous auxiliary solvents are unnecessary for aerosol formulations. It also has better knock-down characteristics than DDT so that auxiliary knock-down agents are also unnecessary. These points are important because aerosol formulations are usually limited to a total of 15 wt. per cent non-volatile materials, which include the insecticide, knock-down agents, auxiliary solvents and mineral spray oils.

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It is especially surprising to find that the product of this invention is of the same order of insecticidal activity as DDT in view of the fact that it is well known in the art that in DDT type compounds the presence of even one additional substituent on the benzene ring, in addition to the one in the 4 position, causes a diminution of activity. Other compounds similar in structure to the applicant's and even those differing only slightly in the nature of the benzene ring substituents were tested and showed distinctly less activity than the applicant's ingredients.

The following examples are given to illustrate this invention, and include both the preparation of the reaction product of this invention and test results on its use for the indicated purposes:

EXAMPLE 1

Ortho-ethoxy toluene

A three way flask equipped with a stirrer, a return condenser, a thermometer and a dropping funnel, was charged with 80 gms. (2 moles) of sodium hydroxide, 800 ml. of water and 216 gms. (2 moles) of ortho cresol. The dropping funnel was charged with 303 gms. (2 moles) of diethyl sulfate. The mixture was cooled to 17° C. whereupon the diethyl sulfate was added slowly to the reactor with stirring and sufficient cooling to keep the temperature below 25° C. All the diethyl sulfate was added over a period of about 20 minutes. Stirring was continued for 1¾ hours, during which time the temperature rose to 40° C. At this point, 25 ml. of 25% sodium hydroxide was added and the mixture was refluxed with stirring for three and one-half hours. The mixture was then cooled and extracted with diethyl ether. The ether extracts were combined, washed, and dried over sodium sulfate. On removal of the ether on the steam bath 198 gms. of a red oil was obtained as a residue. The oil was distilled under 50 mm. pressure, yielding the fractions indicated below:

The first fraction boiled between 100 and 108° C., and weighed 16.8 gms. This was discarded.

The second fraction, the ortho-ethoxy toluene, boiled at 107° C. to 111° C., and weighed 167 gms. It consisted of an almost colorless liquid. The undistilled residue consisted of 10.8 gms. of dark red oil. This too was discarded.

Final product

The trichloro-derivative was prepared as follows:

A 3-way flask equipped with a stirrer, a return condenser, a thermometer and a dropping funnel was charged with 40.8 gms. (0.3 mole) of the ethoxy toluene described above, 24.8 gms. chloral hydrate, and 17 cc. of glacial acetic acid. The dropping funnel was charged with 51 cc. of concentrated sulfuric acid. The latter was then added to the reactor slowly over a period of 22 minutes. Sufficient cooling was employed to keep the reaction temperature below 35° C. during the addition of the acid.

When all the sulfuric acid had been added, the mixture was stirred for one hour at room temperature. At this point the product was poured into ice and water and was extracted with ether. The extract was washed with water and dried over sodium sulfate. The solvent was finally removed under reduced pressure at 40° C. The residue consisted of 55.7 gms. of yellow oil. The latter was evaluated as an insecticide without any further purification.

Chloral can be employed instead of chloral hydrate to obtain the same reaction products.

EXAMPLE 2

The products of this invention were tested for parasiticidal activity. The values given in column I of the following table represent the percentage mortality of the test insects after 96 hours following a two-minute immersion in an 0.25% aqueous solution or suspension of the test product.

The results in column II are given as percent mortality of the test insect after 96 hours following bloodstream injection of 0.002 cc. of a 5% solution of the test product.

The figures in column III list the results obtained on the Nelson Drop Test for house-fly toxicity. At full dosage, D, 5 mg. of test material/gm. body weight is placed in the fly's body (0.002 cc. of a 5% solution per fly). Standards: 0.01 mg. DDT/gm. gives 65% kill (0.002 cc. of a 0.01% solution per fly.). 0.038 mg. pyrethrin/gm. gives 40% kill (0.002 cc. of an 0.038% solution per fly.).

Not all tests were performed on each product. The blank spaces indicate that that particular test was not performed.

The product of this invention is indicated by Formula I above, and an analogous product by Formula II above. Both of these formulae are to be understood, of course, to constitute mixtures primarily of isomers with each of the indicated benzene ring substituents occurring in the para position as discussed above, and the other substituent occurring ortho thereto.

It should be noted from the results obtained that the reaction product of this invention was many times superior to the analogous product indicated by II, about as good as DDT in activity and superior to pyrethrin on the Nelson Drop test.

EXAMPLE 3

The products of this invention were tested for housefly toxicity and knockdown strength on the Peet Grady test. The general test is fully described in the 1940 "Blue Book," published by the publisher of "Soap and Sanitary Chemicals" periodical, on pages 193 to 197, as the large group method. Briefly, the test as practiced consists of releasing 100 to 150 flies in an air-conditioned case 6x6x6 feet and syraying them with 6 ml. of insecticide. After exposure the number of flies which are incapacitated or "knocked down" is noted and all flies transferred to a cage and allowed to recuperate in fresh air for 24 hours, when the dead flies are counted. The results follow:

Peet Grady insecticide test

Composition	Percent of Houseflies down in—					Percent Kill, 24 hrs.
	2 min.	4 min.	6 min.	10 min.	15 min.	
99.8 wt. percent sulfuric acid treated kerosene containing dissolved 0.2 wt. percent reaction product of o-ethoxy toluene and chloral hydrate.	2.5	3	5.2	39	87	87
Official test insecticide	74.0	85	90	96	84	84

The fact that the products of this invention exhibit superior knockdown characteristics than the test insecticide should be particularly noted. This is especially surprising in view of the well known inadequate knockdown strength of DDT and other related compounds.

By virtue of its solubility in the chloro-fluoro-

Compound	Column I.—Contact Insecticidal Activity, Percent Kill		Column II.—Bloodstream Insecticidal Activity, Percent Kill—*Periplaneta americana* (American Roach)		Column III.—House-Fly Toxicity, Nelson Drop Test, Percent Kill
	Blatella germanica (German Roach) A	*Omelpeltus sociatus* (Milk Weed Bug) B	Female A	Male B	
I. $Cl_3CCH\left(\text{C}_6\text{H}_3(OC_2H_5)(CH_3)\right)_2$	75	100	100	100	D/5–100 D/100–100 D/200–100 D/500–50
II. $Cl_3CCH\left(\text{C}_6\text{H}_3(C_5H_{11})(OH)\right)_2$	5	75	40	100	D/1–5
III. DDT	100	100	100	100	D/100–100 D/500–65 D/1000–50
IV. Pyrethrin					D/132–40

methanes "Freons," i. e. CCl_3F, CCl_2F_2, $CClF_3$, $CHCl_2F$ etc., the reaction product from the condensation reaction between chloral hydrate and o-ethoxy toluene is adapted for use in aerosol compositions for space spray and fumigation applications. When put up in this form it can be dispensed in the conventional pressure containers known in the art. The active ingredient is present in an amount of about 1 to 5 wt. percent, and preferably 2 to 4 wt. percent.

For certain insecticidal purposes it is desirable to incorporate mineral spray oils in the aerosol formulations. These relatively non-volatile oils are added to the compositions indicated in the preceding paragraph up to a weight percent concentration of 15%, which represents the combined figure for the mineral spray oil and active insecticide.

The preferred mineral spray oils are the petroleum white oils or lubricating oil fractions such as medium or light lubricating oils, transformer oil, machine oil, deodorized kerosene, etc. The preferred mineral spray oil utilized in the aerosols is a sulfuric acid treated odorless kerosene.

The sulfuric acid-treated kerosene which may be utilized in the aerosols of this invention is also known as "Bayol D" and "deodorized kerosene." Its preparation, i. e., by treating kerosene with fuming or concentrated sulfuric acid, is well known in the art. This acid treated kerosene has a specific gravity in the range of 0.775–0.825, a boiling point predominantly in the range of 400°–505° F., and is substantially free of aromatics, i. e. contains only a trace. A typical inspection is as follows:

Specific gravity	0.775–0.825
A. S. T. M. dist., °F.:	
I. B. P.	400
F. B. P.	505
Mixed aniline point, °F.	175
Flash point, °F	160
Unsulfonated residue, per cent	97
Sulfur, lamp	0.02
Color, Saybolt	25
Per cent aromatics	Trace

A typical three-component formulation is thus as follows:

2–4 wt. per cent of the reaction product from the condensation reaction between chloral hydrate and o-ethoxy toluene.
2–11 wt. per cent sulfuric acid treated kerosene.
"Freon" q. s. (ad 100).

It is particularly preferred to utilize mixtures of "Freons" such as trichloro-mono-fluoromethane, and dichloro-di-fluoromethane.

It is to be understood that the invention is not limited to the specific examples which have been offered merely as illustrations, and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. An insecticidal composition of superior knockdown characteristics consisting of a homogeneous liquid solution of a compound selected from the group consisting of 1,1,1,-trichloro-2,2-(4,4' - diethoxy - 3,3' - dimethyldiphenyl)-ethane and 1,1,1-trichloro-,2,2-(3,3'-diethoxy - 4,4'-dimethyldiphenyl)-ethane in a chlorofluoromethane.

2. A composition as in claim 1, in which the chlorofluoromethane is di - chloro - di - fluoromethane and the reaction product is present in an amount of from 2 to 4 weight per cent.

3. An insecticidal composition of superior knockdown characteristics consisting of a compound selected from the group consisting of 1,1,1-trichloro - 2,2 -(4,4'- diethoxy - 3,3'- dimethyldiphenyl) - ethane and 1,1,1 - trichloro-,2,2-(3,3'-diethoxy-4,4'-dimethyldiphenyl)-ethane, a chloro-fluoromethane and a mineral spray oil.

4. A composition as in claim 3, in which the mineral spray oil is a sulfuric acid treated kerosene, said acid treated kerosene having a specific gravity in the range of 0.775 to 0.825, a boiling point predominantly in the range of 400 to 505° F., and being substantially free of aromatics.

5. An insecticidal composition of superior knockdown characteristics consisting of a compound selected from the group consisting of 1,1,1-trichloro-,2,2-(4,4' - diethoxy - 3,3' - dimethyldiphenyl) - ethane and 1,1,1 - trichloro-,2,2-(3,3'-diethoxy - 4,4' - dimethyldiphenyl) - ethane, trichloro-mono-fluoromethane, di-chloro-di-fluoromethane, and a sulfuric acid treated kerosene, said acid treated kerosene having a specific gravity in the range of 0.775 to 0.825, a boiling point predominantly in the range of 400 to 505° F. and being substantially free of aromatics.

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