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2,879,284

ODOR REMOVAL AND STABILIZATION OF PHOSPHATE-CONTAINING PESTICIDES

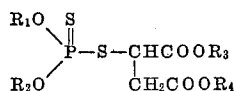
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9 Claims. (Cl. 260—461)

This invention relates to odor removal and stabilization of normally odoriferous phosphate-containing pesticides. More particularly, it relates to the deodorization and stabilization of technical grade dithiophosphate pesticides derived from dithiophosphoric acids.

Dithiophosphate insecticides of the type with which the present invention is concerned are usually esters and may be represented by the general formula:



in which R_1 , R_2 , R_3 and R_4 are selected from the group consisting of aliphatic and aromatic hydrocarbon radicals. Such esters are well known and may be conveniently prepared by reacting O,O-dialkyl dithiophosphate with a dialkyl maleate as described and claimed in United States Letters Patent No. 2,578,652. A typical ester is O,O-dimethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate which is commercially available as "Malathion." While the deodorization and stabilization of this typical ester is principally exemplified in the following description, it is to be understood that any such dithiophosphate ester can advantageously be treated by the process of the present invention.

Unfortunately, technical grade dithiophosphate pesticides as presently manufactured carry an odor sufficiently obnoxious to deter their use for household purposes. When expedients, as, for example, steam distillation and recrystallization, are employed for the removal of mal-odor from dithiophosphate insecticides, such expedients have not proven wholly successful. Notwithstanding the difficulty in carrying out these purifications, it is observed that a steam distilled or a recrystallized but typical O,O-dimethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate refined product is not storage-stable but develops a strong noxious odor after several months of storage. To the present, there is lacking a simple, inexpensive and expeditious process for removing and stabilizing odor found in technical grade or refined dithiophosphate esters.

It is an object of the present invention to provide a process for the removal of obnoxious odors from technical grade dithiophosphate-containing insecticides. It is a further object to stabilize a refined dithiophosphate-containing insecticide to noxious odor development. It is a still further object to provide a premium dithiophosphate-containing insecticide for use in the household. Other objects and advantages will appear from the ensuing detailed description.

To this end, dithiophosphate-containing insecticides are treated with small amounts of either a single peroxide, or a single hydroperoxide or mixtures thereof. The latter peroxide or hydroperoxide compound may be either organic or inorganic. Illustrative compounds included are as follows:

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2,2-bis(tert.-butylperoxy) butane
Cumene hydroperoxide
di-tert.-Butyl peroxide
Pinene hydroperoxide
5 Butyl-pentamethylethyl peroxide
tert.-butyl Hydroperoxide
Hydrogen peroxide
Benzoyl peroxide

10 It is a particular advantage of the present invention that a small amount of a peroxide or a hydroperoxide can be added either directly to a technical grade dithiophosphate-containing insecticide or during dithiophosphate manufacture. In either procedure, the treating agent need not be removed from the dithiophosphate ester. In general, treating agent in a weight range of from about 0.01% to about 1.0% is suitably added to the technical grade insecticide. This amount is insufficient to react with the dithiophosphate. The temperature of admixture may vary between about 15° C. and 60° C., and preferably between 20° C. and 30° C. In general, the treating agent and dithiophosphate are admixed for a relatively short period of time. Advantageously, no more than about 30 minutes is required to obtain an insecticidal composition suitable for household purposes.

Surprisingly, mal-odors substantially vanish from dithiophosphate-containing insecticides which become storage-stable against odor development. The process of the present invention makes possible the utilization for household purposes of highly desirable, but normally malodorous, commercially available dithiophosphate-containing compounds.

The term "substantially odorless" composition as used in the description and claims means a substance which is acceptable by a user for household purposes. Stated otherwise, the product contains little or no odor. Such a product is known as premium grade. All other grades are known as technical grades.

In order to facilitate a further understanding of the invention, the following examples are given primarily for the purpose of illustrating certain more specific details thereof. The scope of the invention is not to be deemed limited thereby, except as defined in the claims. Unless otherwise noted, the parts are by weight.

Example 1

To 1000 parts of technical grade O,O-dimethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate, commercially available as "Malathion," is added 0.5 part (0.05%) of cumene hydroperoxide at a temperature of approximately 25° C. The components are admixed for about 15 minutes. A premium grade of O,O-dimethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate is recovered.

Example 2

To 500 parts of technical grade O,O-diethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate are added 1.25 parts (0.25%) of di-tert.-butyl peroxide and stirred for about 20 minutes. The noxious odor originally present in the dithiophosphate is removed and a premium grade O,O-diethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate is recovered.

Example 3

To 1000 parts of technical grade O,O-dimethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate are added 1.2 parts (0.12%) of pinene hydroperoxide and stirred for 10 minutes. The mal-odor originally present in the dithiophosphate insecticide composition soon disappears. A premium grade O,O-dimethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate insecticide, formerly unsuitable for indoor use, is recovered.

Example 4

To 1000 parts of technical grade O,O-diethyl-S-(1,2 dicarbomethoxyethyl)-dithiophosphate are added 10 parts of tert.-butyl hydroperoxide and stirred for 10 minutes. A premium grade O,O-diethyl-S-(1,2-dicarbomethoxyethyl)-dithiophosphate is recovered, as in Example 3.

Example 5

To 100 parts of technical grade O,O-diethyl-S-(1,2-dicarbophenoxyethyl)-dithiophosphate is added 0.01 part (0.01%) butyl-pentamethylethyl peroxide and stirred at 35° C. for about 15 minutes. The original dithiophosphate is a viscous brown noxious-smelling liquid which is unsuitable for indoor household purposes. After treatment, a premium grade dithiophosphate is recovered.

Example 6

To 100 parts of technical grade O,O-dimethyl-S-(1,2-dicarbethoxyethyl)-dithiophosphate is added aqueous hydrogen peroxide containing active 0.25% hydrogen peroxide and admixed for 10 minutes at room temperature. Two immiscible layers are formed on standing. One layer is aqueous and the other is oily. The aqueous layer is separated and discarded. The oily layer containing premium O,O-dimethyl-S-(1,2-dicarbethoxyethyl)-dithiophosphate may, if desired, be steam stripped.

Example 7

1000 parts of O,O-dimethyl-S-(1,2-dicarboethoxyethyl)-dithiophosphate, which has been previously treated and purified by recrystallization, is stored in a rubber-stoppered container for six months. An obnoxious odor develops. To the so-stored recrystallized dithiophosphate containing a noxious odor is added 0.5 part of cumene hydroperoxide for about 10 minutes. The addition of the cumene hydroperoxide renders the dithiophosphate substantially odorless and storage-stable, even when the dithiophosphate so treated is stored for at least six additional months.

Example 8

To 1000 parts of technical grade O,O-dimethyl-S-(1,2-dicarbethoxyethyl)-dithiophosphate is added 0.5 part (0.05%) of cumene hydroperoxide at a temperature of approximately 25° C. These components are stirred and warmed to about 50° C. for about 15 minutes. The odor of the technical grade dithiophosphate noticeably altered to a premium grade composition singularly suitable for use for household purposes.

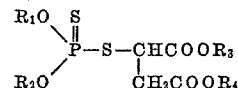
Example 9

To 1000 parts of technical grade O,O-dimethyl-S-(1,2-dicarbethoxyethyl)-dithiophosphate is added 0.25 part (0.025%) of cumene hydroperoxide, 0.25 part (0.025%) pinene hydroperoxide, and 0.25 part (0.025%) of di-tert-butyl peroxide at a temperature of approximately

25° C. The components are all admixed and gradually warmed to 50° C. in about 15 minutes. The odor of the technical grade dithiophosphate noticeably altered to a premium grade composition, as in Example 8.

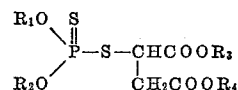
We claim:

1. A method for the odor removal and stabilization of a malodorous pesticide represented by the formula:



in which R₁, R₂, R₃ and R₄ are each selected from the group consisting of aliphatic and aromatic hydrocarbon radicals which comprises adding thereto from about 0.01% to about 1.0%, by weight of a peroxide.

2. A method for removing noxious odors from a dithiophosphate-containing compound which comprises: treating a technical grade dithiophosphorous-containing pesticide represented by the formula:



in which R₁, R₂, R₃ and R₄ are each selected from the group consisting of alkyl and aryl hydrocarbon radicals, from about 0.01% to about 1% by weight of a peroxide selected from the group consisting of cumene hydroperoxide, di-tert-butyl peroxide, pinene hydroperoxide, tert-butyl hydroperoxide, hydrogen peroxide, and mixtures thereof.

3. The process according to claim 2 in which the peroxide is di-tert.-butyl peroxide.

4. The process according to claim 2 in which the peroxide is cumene hydroperoxide.

5. The process according to claim 2 in which the peroxide is pinene hydroperoxide.

6. The process according to claim 2 in which the peroxide is tert.-butyl-pentamethylethyl peroxide.

7. The process according to claim 2 in which the peroxide is hydrogen peroxide.

8. The process according to claim 2 in which the dithiophosphate is technical grade O,O-dimethyl-S-(1,2-dicarbethoxyethyl)-dithiophosphate.

9. The process according to claim 2 in which the dithiophosphate is recrystallized O,O-dimethyl-S-(1,2-dicarbethoxyethyl)-dithiophosphate.

References Cited in the file of this patent

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(As abstracted in Chem. Abstr., vol. 50, 3704a.)