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## PESTICIDAL COMPOSITION

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5 Claims. (Cl. 167—22)

My invention relates to new pesticidal compositions, and more specifically to compositions containing 1,1-dichloro-1-nitroalkanes, which are especially useful as fumigants, particularly for insecticidal or larvicidal applications.

A great many materials have been found to have some insecticidal or larvicidal activity when employed as fumigants, but most of these have been undesirable from a practical standpoint. Some of the most effective fumigants are extremely toxic to human beings, and their use is thus necessarily severely limited. Of the materials which are less toxic to human beings, nearly all have serious disadvantages such as fire or explosion hazards, poor penetrating power, long retention by objects fumigated, and similar undesirable characteristics. For example, chloropicrin, which is a very effective fumigant, is relatively non-toxic to human beings in fumigating concentrations, but is nevertheless a lachrymatory material and is extremely irritating and difficult to handle. It is necessary to wear gas masks when fumigating with chloropicrin, even when the material is handled in the liquid state. Chloropicrin also does not have as high penetrating ability as is desirable, and tends to remain for long periods of time in the materials fumigated. Since even traces of chloropicrin are irritating, this retention of the material by fumigated articles is extremely undesirable.

I have now discovered that the 1,1-dichloro-1-nitroalkanes are extremely efficient fumigating agents and possess practically none of the disadvantages of fumigants previously employed. These materials are non-lachrymatory and non-irritating in the residual concentrations encountered in fumigating work carefully and safely carried out. In spite of the apparently innocuous character of these compounds, as compared to the lachrymatory and irritating chloropicrin, these compounds have comparable insecticidal activity and, in fact, the fumigant activity of chloropicrin is exceeded by 1,1-dichloro-1-nitroethane. For most fumigant uses, I prefer to use this compound or its adjacent homolog 1,1-dichloro-1-nitropropane. However, all of the 1,1-dichloro-1-nitroalkanes exhibit pesticidal activity, and those of sufficient volatility may, of course, be employed as fumigants.

The lower 1,1-dichloronitroalkanes, which are suitable for use as fumigants, are volatile liquids having boiling points within the range of other volatile liquids having fumigant activity (U. S. Dept. of Agriculture Bulletin No. 162). For example, 1,1-dichloro-1-nitroethane boils at 124° C., 1,1-dichloro-1-nitropropane boils at 147.5° C., 1,1-dichloro-1-nitro-2-methylpropane boils at 166.3° C., and 1,1-dichloro-1-nitrobutane boils at 168° C. These compounds also have sufficiently low inflammability to be safely used as fumigants. These compounds may be made by any suitable procedure as, for example, by nitrating the corresponding dichloro compounds or by chlorinating the corresponding nitro compounds. A suitable chlorination process is described in co-pending application Serial No. 242,412 by H. B. Hass et al., which has matured into Patent Number 2,256,839, dated September 23, 1941. For insecticidal purposes these compounds need not be prepared in an extremely pure state, but may be employed as crude reaction products. Since these compounds have relatively mild odors, it is often desirable to incorporate a warning agent in them for fumigant use. Impurities present in the crude product may serve as warning agents; for example, in the chlorination of nitroethane, if a trace of nitromethane is present, some chloropicrin will be produced and even a trace of this latter product in the resulting 1,1-dichloro-1-nitroethane will serve as a warning agent.

When employed as fumigants, my new insecticides have the necessary property of being non-injurious to the usual articles fumigated. For example, in tests with 1,1-dichloro-1-nitroethane, at a concentration of one pound per thousand cubic feet of space for a period of twenty-four hours, no injury whatever was noted on various types of natural and synthetic fabrics either unbleached or dyed with a wide variety of dyes. Similarly, a wide variety of furs, both natural and dyed, showed no injury from this treatment. Likewise, no injury was noted in the case of ninety different patterns of wallpaper in various colors or in the case of other printed matter employing both black and colored inks. Clear and colored Cellophane, black leatherette, and various colored oilcloth samples likewise exhibited no injury. No damage was indicated in a similar test on a number of different kinds of woods finished with varnishes, lacquers, and paint, both clear and colored. In a single case, one paint became temporarily somewhat tacky but quickly recovered its original conditions. Tests on iron, zinc, brass, copper, cadmium, lead, nickel, and silver showed no injury with the exception that at high humidities some corrosion of iron was noted.

When the above fumigating test was applied to perishable products, it was found that very few of

these materials were damaged to any extent. No injury was observed in the case of thirty-five staple food products including meats, eggs, fish, fats, dairy products, cereals and cereal products, dried fruits, canned fruits, potatoes, sugar, coffee, cocoa, etc. Surface injury was noted in the case of some fresh fruits and vegetables, and my new insecticides are not recommended as fumigants for such products. There was no observable damage in the case of eggs, but hatchability was decreased. On the other hand, a number of different types of seeds were fumigated with little effect on germination. These seeds showed the average per cent germination of any fumigated seeds. Various tobacco products were fumigated with no observable injury, and cigarettes smoked some hours after fumigation showed no traces of taste or odor of the fumigant.

A particular advantage of my new insecticides in fumigant application is their penetrating power. This is illustrated by 100% kill of meal worm larvae using 1,1-dichloro-1-nitroethane in a concentration of one pound per thousand cubic feet of space for twenty-four hours with the meal worm larvae in the following environments:

1. In the center of a 100 pound bag of wheat.
2. In the center of a 5 pound bag of white flour.
3. In the center of packages of cereal breakfast foods.
4. In the center of a roll of non-absorbent cotton. Penetration was through a two to three inch layer of tightly packed cotton.
5. In paper containers (seed packages).
6. In sealed mailing tubes.
7. At a depth of seven inches in moderately packed soil of average moisture.
8. In a jar sealed with aluminum foil in which was punched a minute pin hole. In a similar jar sealed by aluminum foil but without a pin hole, a kill of 0% was observed.

The improved penetrating power of my new fumigant may also be seen from a comparison of 1,1-dichloro-1-nitroethane and chloropicrin. Using these fumigants in a 25 cubic foot fumigating chamber at a concentration of 3 pounds per thousand cubic feet for 3 hours, the following results were obtained:

*Table I*

| Insect | Environment of insect | Fumigant | Kill |
|---|---|---|---|
| | | | *Percent* |
| Rice weevil | Center of bag of wheat | Chloropicrin | 82 |
| | | D. C. N. E.* | 100 |
| Do | Center of bag of flour | do* | 85 |
| | | | 100 |
| Carpet beetle larvae. | Hollow in double plug of chewing tobacco. | do* | 0 |
| | | | 100 |

*D. C. N. E.=1,1-dichloro-1-nitroethane.

Another outstanding advantage of my new insecticides in fumigant use is the fact that, in spite of their high penetrating power, they are not retained for a long period by the articles fumigated. Here again a comparison with chloropicrin illustrates this advantage. A 100 pound bag of wheat was fumigated in a 25 cubic foot chamber by means of chloropicrin at a concentration of 3 pounds per one thousand cubic feet for 3 hours. At the conclusion of the fumigation, the air in the chamber was changed by means of exhaust fans, effecting 140 changes of air in a period of approximately 2 hours. The chamber was then allowed to stand closed for 10 hours after which it was opened, and was found to contain a distressing amount of chloropicrin. It was immediately closed, and the air was changed 480 times in the next two hours, at the end of which time a white mouse was placed in the chamber behind an observation window. At the end of an hour, the mouse showed marked symptoms of distress which increased during the next hour. Observations were then discontinued until 15 hours later at which time the mouse was found to be dead. When fumigating with 1,1-dichloro-1-nitroethane at the same concentration and for the same time, the fumigating chamber could be opened at each of the times specified in the above experiment, without any distressing effects.

When employing my new insecticides as fumigants, the same procedures may be employed as have been used with other volatile liquid fumigants. These fumigants are, of course, most effective in a closed space, but they may also be employed in open application such as in soil fumigation and the like. When fumigating in closed spaces, the concentration of the fumigant which must be employed will, of course, depend upon the particular insects to be killed, the time of contact, and the nature of the object being fumigated. Thus, when employing the fumigant in a chamber containing no absorbent material, insects are killed in much shorter time or at lower concentrations of fumigant than when fumigating in a chamber containing an absorbent material such as grain. The concentration and the time necessary for any particular application may be judged by one skilled in the art from the data with respect to 1,1-dichloro-1-nitroethane such as those given in Table II below. This table shows the time required for 100% kill of meal worm larvae in two quart jars filled with grain, and in empty two quart jars for different concentrations of fumigant.

*Table II*

| Environment of insects | Concentration of 1,1-dichloro-1-nitroethane | Time required for 100% kill |
|---|---|---|
| | *Lb./100 cu. ft.* | *Hours* |
| Empty jar | 0.25 | 7 |
| | 0.5 | 3 |
| | 1.0 | 2 |
| | 1.5 | 1 |
| Jar full of grain | 1.0 | 12 |
| | 1.5 | 7 |
| | 2.0 | 6 |
| | 2.5 | 5 |
| | 3.0 | 3 |

The homologs of 1,1-dichloro-1-nitroethane are in general, less toxic to insects than the latter compound. For example, in 24 hour tests using meal worm larvae in empty two quart jars, 1,1-dichloro-1-nitroethane will give 100% kill at a concentration of 0.17 pound per one thousand cubic feet, whereas, 1,1-dichloro-1-nitropropane requires a concentration of 0.33 pound per one thousand cubic feet. Similarly in two quart jars filled with wheat in which the meal worm larvae are buried, 1,1-dichloro-1-nitroethane requires a concentration of less than one pound per one thousand cubic feet to give 100% kill, whereas 1,1-dichloro-1-nitropropane requires a concentration of 2.5 pounds per one thousand cubic feet. Corresponding corrections for the concentrations of other 1,1-dichloro-1-nitroalkanes can be made by those skilled in the art on the basis of simple preliminary tests.

It is to be understood, of course, that the above

examples of fumigant uses of 1,1-dichloro-1-nitroethane and 1,1-dichloro-1-nitropropane are merely illustrative and do not limit the scope of my invention. As has previously been pointed out, other 1,1-dichloro-1-nitroalkanes may be employed as fumigants with proper modification of concentration and time, and it is also evident that there are numerous other fumigant applications of these compounds as well as those particularly illustrated above. Various modifications of the fumigating procedures may also be employed in accordance with prior practices in this regard. For example, these fumigants may be used in conjunction with other fumigants or may be used with diluents such as acetone or carbon tetrachloride, instead of being used alone as in the examples given. Other pesticidal applications of these compounds, as, for example, in rodent control, and insecticidal applications of these compounds other than fumigant uses, will also be apparent to those skilled in the art. In general, it may be said that the use of any equivalents or modifications of procedure, which would naturally occur to those skilled in the art, is included in the scope of my invention.

My invention now having been described what I claim is:

1. An insecticidal composition comprising a lower 1,1-dichloro-1-nitroalkane.

2. An insecticidal composition adapted for use as a fumigant, comprising a 1,1-dichloro-1-nitroalkane containing from 2 to 4 carbon atoms.

3. An insecticidal composition adapted for use as a fumigant, comprising 1,1-dichloro-1-nitroethane.

4. An insecticidal composition adapted for use as a fumigant, comprising 1,1-dichloro-1-nitropropane.

5. An insecticidal composition adapted for use as a fumigant, comprising a 1,1-dichloro-1-nitrobutane.

HENRY B. HASS.

CERTIFICATE OF CORRECTION.

Patent No. 2,281,239. April 28, 1942.

HENRY B. HASS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 47, Table II, for "Lb./100" read --Lb./1000--$^2$; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 14th day of July, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

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