United States Patent Office

2,968,591

Patented Jan. 17, 1961



2,968,591

# CONTROL OF CIGARETTE BEETLES WITH VAPOR OF DDVP

Ralph L. Tracy, Miller Place, N.Y., assignor to Norda Essential Oil and Chemical Company, New York, N.Y., a corporation of New York

No Drawing. Filed May 8, 1957, Ser. No. 657,733

6 Claims. (Cl. 167—22)

This invention relates to a process for the control of insects which damage leaf tobacco and tobacco products in storage, and, more particularly, to a method for the control of the cigarette beetle by subjecting the same to the vapors of a dialkyl halovinyl phosphate.

The cigarette beetle, *Lasioderma serricorne* L., is one of the two major scourges of cured tobacco in the United States. This insect is a tiny dark brown beetle not much larger than a pinhead. It and the tobacco moth are responsible for an annual loss to the tobacco industry estimated to range from $5,000,000 to $20,000,000.

Subject to attack by the cigarette beetle are flue-cured tobacco, Turkish tobaccos, all cigar tobaccos (wrapper, binder and filler types), sun-cured tobacco and many kinds of manufactured tobacco products. It also will infest and occasionally damage dark-fired tobacco. In addition to these, it will breed in many seeds, cereal products, spices, stock feeds, cottonseed meal, upholstered furniture, broom corn and many other materials.

The beetle, which is the adult stage, does not eat. The damage is done by the feeding of the larva or worm stage.

The principal difficulty in combating the cigarette beetle arises from the habit of the beetle and of the larvae to burrow deep into the masses of tobacco stored in the warehouses. Here the insect is well insulated from the cold, and it also cannot be reached by contact insecticides. It will not even be hurt by most fumigants, because these are capable of penetrating into the masses of tobacco in only exceedingly small quantities, which are too small to be toxic to the beetle. In most cases, therefore, it is necessary to rely upon attacking the beetle when it emerges from the tobacco, as it frequently will do during a portion of the day. For this, the art has relied upon contact insecticides and upon fumigation. The first are effective, but only when they physically contact the beetle, which is very difficult to accomplish, and therefore a severe limitation. Fumigation has greater potential promise, but again, a promise not realized until now.

It is of course necessary that the fumigant insecticide employed not affect the odor or flavor of the tobacco. Hydrocyanic acid gas, for example, which is commonly used for cigarette tobaccos, cannot be used with cigar tobaccos, because a lingering odor is present for some time following fumigation. Likewise, methyl bromide has the same disability. A mixture of 34% acrylonitrile and 66% carbon tetrachloride has been suggested for use as a fumigant for cigar tobaccos because of the lack of

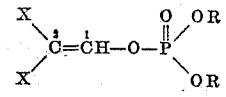


the odor problem. However, Tenhet in Tobacco 139, 12 to 14 (July 16, 1954) reported that it was only reasonably effective, and that the dosage rates tested did not produce mortality of all of the test insects at atmospheric pressure. Vacuum fumigations were more effective, but of course, vacuum fumigation is more expensive, and is not practical for application to an entire warehouse.

Thus, the objective of the art has been to produce an insecticide which is capable of atmospheric fumigation of an entire warehouse with a 100% kill. This ideal, unfortunately, has not yet been realizable. Atmospheric fumigation has not been effective except when used for small lots in atmospheric chambers, which requires the handling of the tobacco bales to insert and remove them in such chambers.

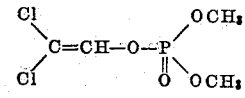
The process in accordance with the invention is capable of achieving a 100% kill of cigarette beetles reached by the insecticide in an entire structure by fumigation in air at atmospheric pressure. Moreover, the treatment of the invention is effective for up to 96 hours if the warehouse is nearly airtight, and ventilation is prevented during that period.

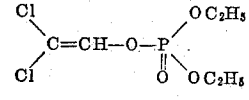
In the process of the invention, there is employed the vapor of an insecticidal compound having the general formula

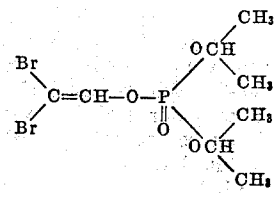


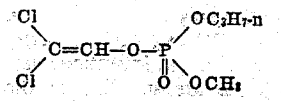
where the X's are halogen, and the R's are alkyl groups having from one to about three carbon atoms. X can, for example, be chlorine, bromine, fluorine or iodine. The R radicals can be straight or branched chain, for instance, methyl, ethyl, propyl, and isopropyl.

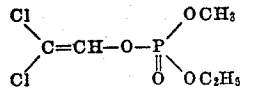
The following compounds are exemplary:

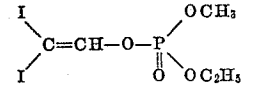


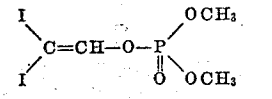


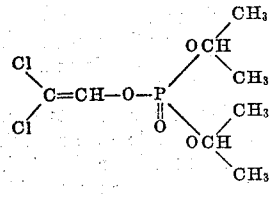


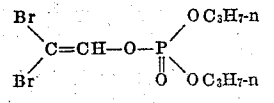


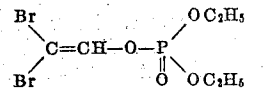


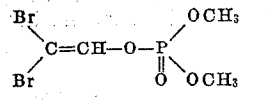


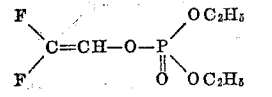


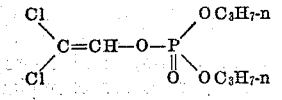


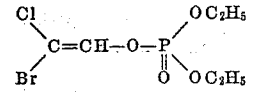


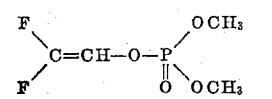












The preferred compound is a dialkyl dichloro vinyl phosphate, for example dimethyl-2,2-dichloro vinyl phosphate, and diethyl-2,2-dichloro vinyl phosphate.

The insecticidal compounds of the invention are known compounds, and can be prepared according to the general procedure outlined by Werner Perkow, Chemische Berichte 87 (5) 755–758 (1954). The procedure there given is for the reaction of a trialkylphosphite such as triethyl phosphite with chloral and bromal, and this procedure is applicable to any of the alkyl phosphites.

In accordance with the invention, vapors of a dialkyl halovinyl phosphate are supplied to the atmosphere in the cigarette beetle infestation zone, in a sufficient concentration to have a toxic or lethal effect. A vapor concentration as low as 5 to 20 micrograms/ft.$^3$ in the air within the structure is lethal, and will effect a 100% kill of insects reached by the vapors when maintained for 24 hours. Larger concentrations than this can of course be used, and because they take longer to dissipate may maintain a highly toxic or lethal atmosphere in a ventilated area over a somewhat longer period; such atmospheres have been maintained for up to 96 hours using an initial 20 micrograms/ft.$^3$. In some warehouses, 10 milligrams/ft.$^3$ has been used successfully. However, it is desirable usually to employ no more than is necessary to produce a 100% kill in the area reached by vapors. Since a toxic or lethal concentration can be maintained longer if the structure is closed, usually the concentration used would be the minimum required for a 100% kill of insects reached by the vapors over a 24-hour period, i.e., within the range from 5 to 20 micrograms/ft.$^3$, and the structure would be kept closed as tightly as feasible.



It is desirable that the cigarette beetle infestation be subjected to a toxic concentration of the dialkyl halovinyl phosphate vapors for a period of at least 24 hours. In many instances, it is prudent to maintain the toxic concentration over a period of from 72 to 96 hours. This can be done even when only the minimum amount of dialkyl halovinyl phosphate is introduced initially, if the atmosphere is kept undisturbed so that dissipation of the vapors of the dialkyl halovinyl phosphate is minimized. For this purpose, the structure which is being fumigated should be sealed, or at least made practically airtight. Vacuum treatment is completely unnecessary in the process of the invention, as has been demonstrated by numerous experiments in which 100% kills of insects reached by the vapors were invariably obtained using the concentration specified over 24-hour periods in ventilated structures and over 72- to 96-hour periods in relatively airtight structures.

The concentrations mentioned are on the basis of the total cubic volume of air within the structure being treated. An amount of dialkyl halovinyl phosphate is introduced within the structure to supply this concentration over the desired fumigation period, which will be at least 24 hours, and as long as desired, depending upon the severity of the infestation, usually up to 72 to 96 hours. The dialkyl halovinyl phosphate can be supplied to the atmosphere by any of several methods.

These compounds are oils, and are slowly volatile at normal atmospheric temperatures.

The compositions can be supplied in the form of sprays, employing solutions or emulsions of the dialkyl halovinyl phosphate in organic solvents and/or in water. Carbon tetrachloride, perchloroethylene, chloroform and deodorized oils, e.g., kerosene, xylene and methylated naphthalenes, as well as isopropyl ether, have been used successfully as solvents. These solvents themselves produce vapors which are quite toxic to the cigarette beetle and bolster the effectiveness of the dialkyl halovinyl phosphate. In addition, these solvents are toxic to the cigarette beetle by direct contact. Sprays would be applied in sufficient amount to disperse and/or deposit within the structure being treated 1 or more microgram/ft.$^3$ of the dialkyl halovinyl phosphate. Conventional spray procedures are limited in use because care must be exercised to avoid spraying the hogsheads per se. Not more than 50 gallons of water emulsion can be used without upsetting the moisture content of the tobacco, and the areas of the floor and wall available for spraying are restricted in the crowded warehouses.

Fogging is an effective method of rapidly dispersing the dialkyl halovinyl phosphate into the atmosphere. About 10 to 12 gallons of deodorized kerosene containing the desired dose of dialkyl halovinyl phosphate is fogged into a warehouse from one or more points. Volatilization of the insecticide occurs in the air permitting

a rapid build-up of insecticidal vapors, which are dispersed relatively evenly throughout the free air space in the warehouse. Only traces of the dialkyl halovinyl phosphate settle onto the hogshead or floor.

A unique procedure of application is simply spilling onto the floor, in the areas conveniently reached by the operator, a solution of the dialkyl halovinyl phosphate. The solvent should be noninflammable and known not to impart odor and taste to tobacco. One or two gallons is sufficient volume for the purpose and any desired dose of the insecticide may be used. Volatilization of dialkyl halovinyl phosphate begins immediately, although insecticidal concentrations are not detected in the atmosphere until about one hour after application.

Of particular importance is this characteristic of the dialkyl halovinyl phosphate to disperse or migrate rapidly in vaporous form throughout the atmosphere. By this behavior it penetrates all free air spaces in, under, and around the hogsheads, creating an effective insecticidal atmosphere for free living beetles and moths. This behavior of dialkyl halovinyl phosphate of permeating the air space of the treated warehouse from a given point of application is not shared by any other organic phosphate insecticide, e.g. tetraethyl pyrophosphate, malathion; the chlorinated insecticides, e.g. lindane, chlordane, and is peculiar to the lowest members of the vinyl phosphate series. Chemically, the dialkyl halovinyl phosphate is a substantial molecule in size (DDVP molecular wt. 221), especially when compared to conventional fumigants, e.g. HCN (molecular wt. 28) or methyl bromide (molecular wt. 95). Also, the vapor pressure of dialkyl halovinyl phosphate is well below the range of those substances. For this reason the dialkyl halovinyl phosphate acts uniquely as a vaporous insecticide, being toxic for insects by direct contact, as is a conventional insecticide, and indirectly toxic by virtue of its fumes, as are the conventional fumigants. In other words, it is a new type of insecticide, intermediate between the volatile ones, i.e., pyrethrins, HCN, etc. and the nonvolatile, residual types, i.e., lindane, malathion, chlordane, TEPP, etc. In the latter case, the dialkyl halovinyl phosphate is well differentiated biochemically from the fumigants by the fact that 1 g./1000 cubic feet of dialkyl halovinyl phosphate is as insecticidally effective as 454 g. of HCN and 780 g. of methyl bromide.

The following examples are illustrative of the process of the invention:

## EXAMPLE 1

Wide-mouthed 4000 ml. (one gallon) glass jars were used as the experimental containers in these laboratory tests. Whatman No. 1 filter papers, 13 cm. in diameter were impregnated with the dilutions given in the tables below, of 2,2-dichloro dimethyl vinyl phosphate (DDVP) in solution in a solution of deodorized kerosene. These filter papers were placed on the bottom of the glass jars, and squares of cheesecloth or copper wire held in place by rubber bands were used as tops. There was no excess or free solution on the surface of the filter paper. Ventilation was relatively free in all jars.

Contact toxicity was determined by placing the beetles directly on the charged filter papers. Vapor toxicity was determined by suspending the beetles in cheesecloth bags in the upper half of the jar.

The following data compares the contact and vapor toxicity of DDVP:

*Table I*

24 hour exposure
25 bettles per test; 8 days old
25° C. and 40% humidity

| Solution DDVP concentration | | Percent killed | | | |
|---|---|---|---|---|---|
| | | Hours of exposure to DDVP | | | |
| Percent W./W. | g./cc. | Contact | | Vapor | |
| | | 24 | 120 | 24 | 120 |
| 50 | 0.5 | 100 | 60 | 90 | 40 |
| 25 | 0.25 | 100 | 50 | 100 | 10 |
| 10 | 0.10 | 100 | 40 | 100 | 10 |
| 1.0 | 0.01 | 100 | 10 | 100 | 0 |
| 0.1 | 0.001 | 100 | 20 | 90 | 0 |
| 0.01 | 0.0001 | 100 | 0 | 80 | 0 |
| Control—No DDVP | | | | | |
| Deodorized kerosene | | 100 | 10 | 40 | 10 |

The above data shows that the vapors of 2,2-dichloro dimethyl vinyl phosphate are sufficiently lethal to effect a 100% kill at concentrations of from 0.25 to 0.01 g./cc. after a 24-hour exposure. However, the vapors are rapidly dissipated and after 120 hours the effectiveness is practically nil. It is noteworthy that the data shows that the effectiveness of the vapor is nearly equal to that of the insecticide when in contact with the insects; this demonstrates the remarkable vapor toxicity of DDVP for the cigarette beetle.

The following data shows the persistence of the DDVP vapors over the period from 1 to 120 hours:

*Table II*

24 hour exposure
15-20 bettles per test; 7-9 days old
25° C. and 35-40% humidity
Solvent—deodorized kerosene

| Solution DDVP concentration | | Percent killed | | | | | | | | Order of kill | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Hours of exposure to DDVP Vapor | | | | | | | | DDVP (g.) | Hrs. | Average percent kill |
| Percent | Grams | 1 | 2 | 4 | 24 | 48 | 72 | 96[1] | 120 | | | |
| 100 | 4.0 | ------ | 80 | ------ | 90 | 100 | 90 | 50 | ------ | ---------- | ------ | ---------- |
| 100 | 2.0 | ------ | 80 | ------ | 80 | 100 | 90 | 10 | ------ | ---------- | ------ | ---------- |
| 100 | 1.0 | ------ | 50 | ------ | 99 | 80 | 100 | 100 | 20 | ---------- | ------ | ---------- |
| 50 | 1.0 | 90 | 60 | 80 | 90 | ------ | ------ | ------ | ------ | ---------- | ------ | ---------- |
| 50 | 1.0 | 99 | 80 | 70 | 100 | ------ | ------ | ------ | ------ | 1-4 | 2 | 70 |
| 50 | 0.5 | ------ | 40 | ------ | 70 | 50 | 100 | 100 | 30 | 1-4 | 24 | 92 |
| 10 | 0.1 | ------ | 50 | ------ | 73 | 50 | 100 | 80 | 10 | 0.5- .1 | 2 | 45 |
| 1.0 | 0.01 | ------ | 10 | ------ | 80 | 50 | 80 | 90 | 20 | 0.5- .1 | 24 | 72 |
| 0.1 | 0.001 | ------ | 10 | ------ | 33 | 50 | 80 | 60 | 10 | 0.01- .001 | 2 | 10 |
| Control—No DDVP | | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | 0.01- .001 | 24 | 56 |
| Deodorized kerosene alone | | 0 | 0 | 0 | 10 | ------ | 0 | ------ | 0 | ---------- | ------ | ---------- |

[1] 48-hour count instead of 24-hour count.

It is noteworthy that the lower concentrations of vapor are lethal after a longer period of exposure. This may be due to build-up of vapor concentration, which required a longer period in view of the lower starting concentration of the 2,2-dichloro dimethyl vinyl phosphate. It is apparent that 4 g. of 2,2-dichloro dimethyl vinyl phosphate is actually no more effective than 1 g. at the end of 24 hours of exposure. The rate of volatilization is constant, forming the same toxic vapor concentration, so that the amount of 2,2-dichloro dimethyl vinyl phosphate in excess of 1 g. actually is wasted at only a 24-hour exposure. The data, however, shows that the 4 g. concentration is the more effective after 96 hours.

Below a concentration of 1 g. of DDVP, the lethal activity in 2 hours is significantly less; at the 0.01 g. level, the toxicity is practically nonexistent. On the other hand, after 24 hours the percent kill by amounts of 0.01 to 0.001 g. is only 10 to 30% less than the percent kill caused by 1 to 4 g., and after 72 hours the percent kill is higher than at the higher concentrations.

Apparently, for a given period of exposure, the toxic effect of the DDVP vapor is not directly proportional to concentration, after a certain threshold level has been exceeded. The rate of dissipation of the vapor appears to be the primary factor which determines the persistence of the insecticidal action of the vapor. Greater weights of 2,2-dichloro dimethyl vinyl phosphate escaped from the test jars of high concentrations within 72 to 96 hours than escaped from the test jars of lower concentrations of 2,2-dichloro dimethyl vinyl phosphate. For this reason, the residual action of the vapors was no greater after 120 hours for doses of 1 g. than for 1 mg.

The practical point of this observation in the case of warehouse fumigation is that attempting to increase the residual period by increasing the weight of 2,2-dichloro dimethyl vinyl phosphate sprayed into the warehouse will not be successful, by itself. The rate of dissipation in the warehouse must be lowered before a more enduring toxic vapor effect is obtained. In other words, the warehouse must be fairly airtight. When this is done, large amounts of DDVP are unnecessary, and the minimum toxic level suffices for a longer period.

It is apparent from the data that vapors from a 1% solution of 2,2-dichloro dimethyl vinyl phosphate in odorless oil will be effective to kill the adult cigarette beetle for at least 3 to 4 days in closed or semi-open quarters.

## EXAMPLE 2

Five tobacco warehouses were fumigated in accordance with the invention with 2,2-dichloro dimethyl vinyl phosphate (DDVP). The tests were carried out by placing nine to twelve small copper screen cages, each containing twenty-five young adult cigarette beetles, in various locations among the bales or hogsheads of tobacco in each warehouse tested. The beetles had been laboratory reared, and were from 1 to 3 days old. In one set of tests the beetles were in place when the warehouses were treated. In two later tests, the warehouses were treated about one hour before the beetles were introduced. Every 24 hours, the exposed beetles were collected and replaced with fresh beetles in new clean cages. In some of the tests the cages were exposed for 48 hours before being removed. A count for dead and live beetles were made 48 hours after collection or, in these cases, from 72 to 96 hours from the start of exposure.

Three warehouses were fumigated by fogging the insecticide at a 2% concentration, using a Tifa apparatus. One warehouse was sprayed with a water emulsion at about 3.5% concentration of 2,2-dichloro dimethyl vinyl phosphate. Only the clear walls, ceiling and floor areas were treated. Those areas obstructed by bales, hogsheads or otherwise were not treated. In two warehouses, 2 and 4 lbs., respectively, of 2,2-dichloro dimethyl vinyl phosphate in solution in carbon tetrachloride were applied to the floors of the runway adjacent to the piles of hogsheads. The operator walked along the runways at a rapid pace, sprinkling the solution onto the floor and to one side, as he progressed, from a 2-gallon garden sprinkling can.

The 2 lbs. was applied in 4 gallons of carbon tetrachloride, and the 4 lbs. was applied in 3 gallons of carbon tetrachloride.

In addition, five white rats 90 days old, both male and female, were placed in the warehouses about one hour after treatment and held there for 7 days. Ample food and water were supplied to them daily. The cages were made of 3/8" mesh galvanized wire. Considerable fog was still present in the warehouses so treated when the animals were initially introduced.

The results of these tests are shown in the following table:

*Table III*

| Warehouse | Type of warehouse [1] | Total lbs. DDVP applied | Method of appln. | Time after treatment, hours | Time beetles exposed | Killed (74-hr. count) |
|---|---|---|---|---|---|---|
| A | Open—16" to 24" air strip around building near ceiling. | 8 | Spray (3.5 water emulsion). | 24 | 24 | 100 |
| | | | | 48 | 24 | 5 |
| | | | | 48 | 48 | 75 |
| | | | | 72 | 24 | [2] |
| B | do | 8 | Fog (2% odorless oil (Deodorized Kerosene) solution). | 24 | 24 | 100 |
| | | | | 48 | 24 | 18 |
| | | | | 48 | 48 | 18 |
| | | | | 72 | 24 | [2] |
| C | Closed—No air strip in building. | 4 | Fog (27% Deodorized Kerosene solution). | 24 | 24 | 100 |
| | | | | 48 | 24 | 100 |
| | | | | 48 | 48 | 100 |
| | | | | 72 | 24 | 100 |
| | | | | 96 | 24 | 100 |
| D | do | 4 | Sprinkled (12.5% $CCl_4$ solution). | 24 | 24 | 100 |
| | | | | 48 | 24 | 100 |
| E | do | 2 | Sprinkled (4.8% $CCl_4$ solution). | 24 | 24 | 100 |
| | | | | 48 | 24 | 100 |

[1] All warehouses had a total air volume of about 250,000 cubic feet. The closed warehouses differed from the open warehouses only in the absence of the air strip or ventilator around the building. No special sealing of these buildings was employed in the above treatments.
[2] None to few.

The data show that in the closed warehouse C a 100% kill of the test insects was obtained for 96 hours after treatment with 4 lbs. of dichloro dimethyl vinyl phosphate. In warehouses D and E, which also were closed, sprinkled with 2 and 4 lbs. of dichloro dimethyl vinyl phosphate, a 100% kill of the test insects was obtained daily for 48 hours after treatment. These two tests were continued for 72 hours beyond the readings recorded, and the verbal reports thereafter indicated that extremely high rates were effected during this additional period.

In warehouses A and B which were left open, excellent results were obtained, 100% kill of the test insects after 24 hours. However, it is apparent that because the warehouses were open the 2,2-dichloro dimethyl vinyl phosphate was rapidly dissipated, so that after 24 hours the kill dropped to from 5 to 75%. This shows the importance of keeping the warehouses closed in order to obtain maximum effectiveness from the fumigation.

In all of the tests the white rats remained healthy and active without exhibiting any suggestion of unwarranted symptoms through their seven days exposure.

The field test shows further that 2,2-dichloro dimethyl vinyl phosphate possesses both a fumigant and a contact insecticidal activity of extremely high potency for the cigarette beetle.

## EXAMPLE 3

A series of experiments were carried out employing the test conditions set forth in Example 2 in four warehouses of 425,000 cu. ft. each. The results showing the mortality of caged cigarette beetles under the test conditions are given in the table below:

*Table IV*

| Test beetles placed in warehouse | Hours in warehouse | Type of warehouse | Method of applying insecticide | Dosage of DDVP in warehouse | Percent kill of test beetles |
|---|---|---|---|---|---|
| Prior to treatment | 24 | Open | Fog [1] | 8 lbs.: 8.5 mg./ft.$^3$ | 100 |
| 24 hrs. after | 24 | | | | 25 |
| 24 hrs. after | 48 | | | | 42 |
| 48 hrs. after | 24 | | | | 13 |
| 72 hrs. after | 24 | | | | 2 |
| Prior to treatment | 24 | Closed | Fog [2] | 4 lbs.: 4.2 mg./ft.$^3$ | 100 |
| 24 hrs. after | 24 | | | | 100 |
| 24 hrs. after | 48 | | | | 100 |
| 48 hrs. after | 24 | | | | 100 |
| 72 hrs. after | 24 | | | | 99 |
| 7 days after | 24 | | | | 85 |
| Prior to treatment | 24 | Open | Residual spray [3] | 1% in 45 gals. water or 3.7 lb. and 4 mg./ft.$^3$. | 100 |
| 24 hrs. after | 24 | | | | 5 |
| 24 hrs. after | 48 | | | | 22 |
| 48 hrs. after | 24 | | | | 2 |
| 72 hrs. after | 24 | | | | 6 |
| 1 hr. after treatment | 24 | Closed | Sprinkled on floor [4] | 4 lbs.: 4.2 mg./ft.$^3$ | 100 |
| 24 hrs. after | 24 | | | | 100 |
| 72 hrs. after | 24 | | | | 100 |
| 1 hr. after | 24 | | | | 100 |
| 24 hrs. after | 24 | | | 2 lbs.: 2.1 mg./ft.$^3$ | 99+ |
| 72 hrs. after | 24 | | | | 18 |
| Control | 24 | | None | None | 1+ |

[1] The amount indicated of 2,2-dichloro dimethyl vinyl phosphate dispersed in 10 gal. of deodorized kerosene
[2] The amount indicated of 2,2-dichloro dimethyl vinyl phosphate in 5 gal. of deodorized kerosene.
[3] Applied to the floor of the aisle on one wall and about one-half of the ceiling. The insecticide contained 1% of 2,2-dichloro dimethyl vinyl phosphate dissolved in tetrachloroethylene and Toximul 500, diluted with 45 gal. of water.
[4] The weight indicated of 2,2-dichloro dimethyl vinyl phosphate dissolved in 3 gal. of carbon tetrachloride.

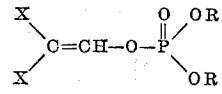
The above data confirms the conclusions expressed in connection with Example 2 as to warehouses of twice the size. When the warehouse is closed, the treatment is effective for a considerable period of time against beetles newly introduced into the warehouse. This is because the vapors are not lost from the warehouse. When the warehouse is ventilated, the effectiveness is limited to about 24 hours.

The process of the invention gives the tobacco industry a method which for the first time makes possible the complete control of the adult cigarette beetle. The ability to kill the beetle by vapor in very low concentrations simplifies the application. Atmospheric fumigation can be effected in structures of any size, and in air, even in ventilated warehouses, with the expectation of a 100% kill of the insects exposed to the vapor over a 24-hour exposed period. A toxic period of up to 120 hours is obtainable at low concentrations merely by making the structure reasonably airtight. No other known atmospheric fumigation process proposed and tried for control of the cigarette beetle has been so effective.

All percentages in the specification and claims are by weight.

I claim:

1. A process for the control of the cigarette beetle *Lasioderma serricorne* L., which comprises subjecting the beetle to an atmosphere comprising a lethal concentration of the vapor of a dialkyl halovinyl phosphate of the formula



wherein each X is halogen, and each R is an alkyl radical having from one to three carbon atoms.

2. A process in accordance with claim 1 in which the concentration is within the range from 5$\gamma$ to 10 mg./ft.$^3$.

3. A process in accordance with claim 1 in which the dialkyl halovinyl phosphate is 2,2-dichloro dimethyl vinyl phosphate.

4. A process in accordance with claim 1 in which the dialkyl halovinyl phosphate is 2,2-dichloro diethyl vinyl phosphate.

5. A process in accordance with claim 1 in which the atmosphere is formed from a fog of a solution of the dialkyl halovinyl phosphate.

6. A process in accordance wtih claim 1 in which the atmosphere is formed from a solution of the dialkyl halovinyl phosphate.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,861,912 | Sallman | Nov. 25, 1958 |
| 2,865,943 | Lorenz | Dec. 23, 1958 |

FOREIGN PATENTS

| | | |
|---|---|---|
| 203,224 | Australia | May 25, 1955 |

OTHER REFERENCES

Carey et al.: Science 118, 28–9, 1953.

Mattson et al.: Agricultural and Food Chem., vol. 3, No. 4, April 1955, pp. 319–321.