

PATENT SPECIFICATION

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(54) DEVICES FOR COMBATING INSECTS

(71) We, A. H. ROBINS COMPANY, INCORPORATED, a Corporation organised and existing under the laws of the State of Virginia, United States of America, of 1407 Cummings Drive, Richmond, Virginia 23220, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the control of insects such as common houseflies (*Musca domestica*), fruit flies (*Drosophila melanogaster*), mosquitoes (*Culex pipiens*) and other similar insects in the vicinity of an insecticide-containing device.

Heretofore, insect-combating devices, such as pest strips and the like, comprised a PVC (polyvinyl chloride) resin having a dispersion of the insecticide dimethyl 2,2-di-chlorovinyl phosphate, commonly known as DDVP or by the trade mark VAPONA, have been widely used for the purpose of controlling flying insects such as houseflies, mosquitoes and the like in the vicinity of the device. DDVP has been reported to have an objectionable depressing effect on the plasma and red cell cholinesterase, at least in animals, which effect is particularly acute at high concentrations which are produced during the first few days after a pest strip has first been exposed to the atmosphere. This is believed due to the fact that the liberation rate of DDVP from presently available DDVP-containing pest strips is not uniform but is higher during the first few days after activation, i.e. removal of the pest strip from the packing and exposing it to the atmosphere. There are also indications that DDVP may be harmful to humans. Pest strips containing DDVP have been banned in the Netherlands. Moreover, the aforementioned initial high liberation rate represents an unduly rapid loss of insecticide and creates an upper limit on the period that DDVP is liberated at a rate sufficient to control pests effectively DDVP also has been found to possess a high degree of residual toxicity in the area of the device, apparently from adsorption of the DDVP vapours in walls, floors, ceilings, curtains, rugs and other articles. Even after a DDVP-containing pest strip has been removed from a room, residual DDVP vapours can often be detected for several days thereafter.

It has also been suggested to utilize other insecticides such as naled (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate) in an insect-combating device such as a pest strip. The preparation of naled is described in United States Patent Specification No. 2,971,882 (Osmonson et al.). PVC resin-naled combinations have been proposed for use as an insecticide of a general nature in French Patent Specification No. 1,568,198 and in British Patent Specification No. 955,350. Netherlands Patent Application No. 66 10279 discloses fly strips composed of PVC-naled as well as PVC-DDVP combinations which are stated to have such high insecticide release rates as to require an outer laminate layer to retard the insecticide release. United States Specification No. 3,344,021 discloses PVC-naled combinations for use as an anthelmintic composition.

A number of problems have been encountered in providing a commercially satisfactory PVC resin-naled combination for use in an insect-combating device. First, there must be a sufficient amount of naled released to provide effective control of the insects in the vicinity of the device. Contrary to statements in the prior art disclosures, it has been found that release rates for naled are very much less than the release rates for DDVP. Naled has a low vapour pressure of about 2×10^{-4} mm Hg at 20°C as compared to that for DDVP of about 1.2×10^{-2} , thus only about 1.7% of the vapour pressure of DDVP.

It has further been found that the inclusion of an insecticide such as naled in a synthetic resin matrix in amounts sufficient to combat insects for a commercially acceptable time leads to exudation of liquid insecticide ("spew") on the surface of the device. These liquid droplets pose serious environmental and aesthetic problems as well as significantly decreasing the effective life of the device.

A further unexpected problem found with a PVC-naled composition was the tendency of the resin to decompose during the shaping process. For example, unsatisfactory results were obtained in early tests where naled was substituted for DDVP in PVC combinations employed in extrusion apparatus used for making PVC-DDVP pet collars known in the art. Burning and charring of the extrudate were found to occur during curing of the collars, and the finished collar underwent an unexplainable reduction in the naled concentration as compared with the naled concentration in the original mixture.

It is an object of this invention to provide an insecticidal combating device and method of using such device which alleviates or avoids the problems of the prior art.

According to one aspect of the present invention a device for combating insects comprises a shaped solid body constituted by a solidified mixture which has been shaped at elevated temperature of a synthetic resinous matrix material, from 15 to 35 weight percent of naled, a minor amount effective to retard spewing of the insecticide of finely divided silica and of at least one C_{14} to C_{20} saturated aliphatic carboxylic acid or salt or ester thereof, and a surface porosity control component that is non-reactive in the mixture and has a boiling point at or below the shaping temperature to produce surface openings in communication with pores in the body by vaporization of the porosity control component to provide for release of naled gas at a rate effective to combat insects in the vicinity of the body but insufficient to form as spew on the body. Thus, the body has a porous surface capable of gradually and continually releasing naled insecticide in an amount sufficient to provide an insecticidally active concentration of naled for a long time.

The body of the device may be flexible and may contain, for example, from 20 to 30 weight percent naled, from 15 to 25 weight percent of finely divided silica particles, from 0.5 to 1.5 weight percent of the acid or salt or ester, and from 1 to 3 weight percent of the surface porosity control component.

According to another aspect of the invention a method of combating insects comprises placing and maintaining a device as aforesaid in an area in which insects are to be combated.

The accompanying drawing is a schematic representation of a preferred embodiment of the invention.

The drawing shows a device embodying this invention, for combating insects. The device illustrated is in the form of a shaped body 1 having a regular, symmetrical matrix of cavities 2 defined by walls 3 and which extend through the body. The cavities have substantially parallel axes that intersect at least one substantially straight line along one dimension of the body. In this fashion, the shaped device has good dimensional stability and is easy to manufacture, and has a large surface area from which the insecticide is released. Other shapes may also be utilized.

The components making up a satisfactory insecticide-containing insect-combating device include a synthetic resin that is compatible with high proportions of insecticide and a strength sufficient to maintain the integrity of the shaped device throughout the period during which the insecticide is released in amounts effective to combat insects, e.g. flies or mosquitoes. The shaped insect-combating device includes the synthetic resin in a concentration sufficiently large to give the device physical properties such as strength flexibility and freedom from tackiness so as to make it suitable for use as an insect-combating device. Generally, the shaped device contains from about 20 to about 80, preferably from about 25 to about 50, weight percent of the synthetic resin.

Various synthetic resins can be used in the insect-combating device, including polyolefins such as polyethylene, polypropylene and copolymers of ethylene and propylene; polyamides such as nylon; regenerated cellulose; polyacrylates such as methacrylate, ethylacrylate, methylmethacrylate and ethylmethacrylate polymers and copolymers; polymers of vinyl compounds such as polystyrene and polymerized divinylbenzene, polyvinyl halogenides such as polyvinylchloride, polyvinylacetate, ethylvinylacetate-vinylacetate copolymers, copolymers of vinylchloride and vinylacetate; polyvinylacetals such as polyvinylbutyral;

polyvinylidene compounds such as polyvinylidenechloride; polyurethanes; polyaldehydes; and thermoplastics.

Polyvinylchloride (PVC) homopolymers and copolymers with other monomers such as vinyl acetate (e.g. PVC—PVA) are preferred synthetic resin materials. Suitable PVC resins are commercially available and include, for example, PVC homopolymer dispersion resin Diamond PVC—7502 and PVC homopolymer extender resin Diamond PVC—7—446, both available from The Diamond Shamrock Co., U.S.A., and mixtures thereof. Other suitable commercially available PVC resins are known in the art. Suitable PVC—PVA copolymers are also commercially available and include, for example, Geon 135 (Goodrich Corp., U.S.A. — GEON is a trade mark), PVC—74 (Diamond Alkali Co., U.S.A.) and XR—6338 (Exxon-Firestone, U.S.A.). Other suitable PVC—PVA copolymers are also known in the art.

The insect-combating device of the present invention contains naled (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate) insecticide in an amount sufficient to provide an insecticidally active concentration of the insecticide over a long period of time (e.g. about 120 days or longer), which amount can be from 15 to 35, preferably from about 20 to about 30, weight percent insecticide. With insecticide concentrations in these ranges, the insect-combating device releases from about 1.5 to about 5 milligrams of insecticide per square inch of surface area per day. Although the insect-combating device of the present invention may be utilized in any environment containing the insects, maximum efficiency may be obtained when the device is utilized in a confined space including these insects.

Generally, the utilization of naled insecticide in amounts of from 15 to 35 weight percent in a synthetic resin matrix leads to liquid naled droplet or "spew" formation on the surface of the insect-combating device. Liquid droplets of naled insecticide forming on the surface of the shaped device pose a substantial health and safety hazard as well as diminished insecticidal efficiency. The insect-combating device of the present invention includes a minor amount effective to retard spewing of the insecticide of finely divided silica particles and of at least one C_{14} to C_{20} saturated aliphatic carboxylic acid or a salt or ester thereof and exhibits a substantially lessened tendency towards formation of liquid droplets of naled insecticide on its surfaces.

Although silica is known in the art, along with a number of other minerals and glasses, as a filler for various synthetic resins, it has unexpectedly been found that finely divided silica particles generally having a particle size of from about 1 to about 50, preferably from about 2 to about 10, microns, exhibit a high degree of relative efficiency in retarding insecticide spewing when utilized in sufficient amounts, which spew-retarding amounts are generally in the range of from 10 to 35, preferably from 15 to 25, weight percent of the insect-combating device. It has been found that utilization of finely divided silica particles in an amount of less than 10 percent by weight is generally ineffective to provide any significant retardation of the insecticide spew while utilization of finely divided silica particles in an amount above 35 percent by weight generally does not result in any further reduction in spew formation.

While the addition of the finely divided silica particles exhibits a high degree of relative efficiency in retarding naled insecticide spewing, a small amount of the naled insecticide may nonetheless sometimes exude from the insecticide-containing device. It has further been found that the inclusion in the device of a minor amount of at least one C_{14} to C_{20} saturated aliphatic carboxylic acid or a salt or ester (e.g., magnesium stearate) thereof, is effective to essentially retard any naled insecticide spewing which might otherwise occur. The C_{14} to C_{20} saturated aliphatic carboxylic acid, which can be a mixture of such acids, is generally utilized in an amount of from 0.25 to 3, preferably from 0.5 to 1.5, weight percent in the device. Stearic acid and palmitic acid are preferred.

While East German Patent 91,898 discloses the addition of a C_{14} to C_{20} saturated aliphatic carboxylic acid along with a particular mixture of primary and secondary plasticizers to a polyvinyl chloride-DDVP mixture, the acid-plasticizers mixture being added to retard spewing of the DDVP, it has been found that the utilization of the C_{14} to C_{20} saturated aliphatic carboxylic acid alone (i.e., without the finely divided silica particles) with the resin and insecticide in the insect-combating device of the present invention is insufficient effectively to retard spewing of the naled insecticide from the device. Similarly, the use of the finely divided silica particles alone (i.e., without the C_{14} to C_{20} saturated aliphatic carboxylic acid) is insufficient effectively to retard spewing of the insecticide from

the device. However, the utilization of a minor amount of both the finely divided silica particles and the C_{14} to C_{20} saturated aliphatic carboxylic acid has been found to possess a high efficiency for insecticide spew retardation and effectively to maintain the surface of the device free of liquid droplets of the insecticide.

It has been ascertained that when the release rate falls off to about 0.4 to about 0.6 milligrams of naled per square inch of surface area per day, the effectiveness of the device for insect control has been reduced to the point where it should be replaced. Utilization of naled in the device in amounts less than about 15 weight percent results in the release rate reaching an ineffective level in a short period of time (e.g., about 90 days or less). Utilization of naled in amounts greater than about 35 weight percent results in spewing and droplet accumulation on the surface of the device.

The preparation of synthetic resin-insecticide combinations is achieved by conventional methods. Because of the compatibility of the insecticide in the resin dispersions, the compositions may be prepared merely by mechanical mixing of the pesticides with powdered resin. Dry blends, fluid pastes, or plastisol dispersions, can be made which, as is known, can be moulded, extruded, cast, or otherwise formed at elevated temperature into the shape of a band or strip. When the prepolymerized resin exists in liquid form, as in the case of such monomers as styrene or methyl methacrylate, the insecticide may be incorporated in the liquid before it is polymerized or cured. The term "dispersion" as used herein is intended to include mixtures of a solid with a liquid, a liquid with a liquid and a solid with a solid.

In the embodiments where polyvinyl resins are used, plasticizers and other additives commonly used for providing the flexibility, strength and surface characteristics desired for an insect-combating device are well known to those skilled in this art, and no further discussion is deemed necessary here. In addition, colouring and odour control agents may be employed in the devices of the present invention to enhance consumer acceptance.

As noted above, naled has a low vapour pressure. The naled release rate from a PVC-naled device is comparatively low and may be inadequate for a commercially acceptable insect-combating device. The use of an additive in the mixture can be very helpful in increasing the naled release rate and makes possible both effective insect control at lower initial naled concentrations and an insect-combating device having an increased effective life.

The additive, also referred to as a surface porosity control component, is present in the final plastisol dispersion or mix used in forming the device, and hence must be non-reactive with the other components of the dispersion or mix. The main function of the additive is to provide a surface porosity which preferably includes pores extending part way into the body of the device. The desired surface characteristics are obtained by the vaporization of the additive during the curing period. Hence the additive should comprise one or more compounds having a boiling point at or below the curing temperature of the resin.

Compounds which are suitable as the surface porosity control component in PVC resins which are cured at a temperature in the range of between about 260° to 400°F include aldehydes and their lower alkyl acetals containing bromine or chlorine, generally having a boiling point in the range from 170° to 400°, preferably from 185° to 350°, F. The porosity control component may thus include one or more of the following which have approximate boiling point temperature as set forth:

Name	B.F. °F
chloroacetaldehyde	185
dichloroacetaldehyde	192
chloral	218
bromoacetaldehyde	176—221
dibromoacetaldehyde	346
bromal	345
bromodichloroacetaldehyde	258
chlorodibromoacetaldehyde	299
bromochloroacetaldehyde	233
2-bromopropanol	229

The surface porosity control component is included in the synthetic resin-
naled combination in an amount sufficient to produce sufficient surface porosity by
its vaporization during curing of the dispersion to effectively increase the release
rate of naled gas from the formed device. While the amount of the porosity control
component to be used depends on the density of surface openings desired and
somewhat on the particular procedure used for curing the resin, it is generally from
about 0.8 to 5, preferably from about 1 to 3, weight percent of the dispersion.

In a preferred form of the invention the body is flexible and contains from 20
to 30 weight percent of naled, from 15 to 25 weight percent of finely divided silica
particles all below 200 mesh size and at least 90% by weight thereof having a
particle size less than 75 microns, from 0.5 to 1.5 weight percent of palmitic or
stearic acid, and from 1 to 3 weight percent of the surface porosity control
component, and the synthetic resin is a polyvinyl chloride resin which has been
formed into the said body from a liquid plastisol dispersion including the surface
porosity control component by filling (e.g. by injection) a casting mould preheated
to a temperature of about 290°F which is thereafter increased to about 360°F (e.g.
in a hot air, radiant heated oven for about two minutes), the body being thereafter
cooled and removed from the mould.

The invention is additionally illustrated by the following Examples.

Example I.

A mixture (in parts by weight) of

- 30 p.b.w. polyvinyl chloride homopolymer dispersion resin
- 16 p.b.w. di-2,ethoxyhexyl phthalate (DOP)
- 2 p.b.w. epoxidized octyl tallate (EPO)
- 1 p.b.w. "Bentone" (a viscosity control agent — BENTONE is a trade mark)
- 27 p.b.w. naled (1,2-dibromo-2,dichloroethyl dimethyl phosphate)
- 3 p.b.w. bromodichloroacetaldehyde
- 20 p.b.w. amorphous silica particles, average particle size, 2.35 microns
- 1 p.b.w. palmitic acid

is thoroughly triturated to form a plastisol dispersion having a viscosity at 25°C of
16,000 cps, as measured on a Brookfield viscometer at 20 rpm., 12,000 at 2 rpm. A
portion of the plastisol is metered to a closed machined aluminium cast mould
having a honeycomb-shaped cavity as in the Figure. Temperature of the mould at
filling time, as indicated by a thermocouple immediately beneath the cavity
surface is 390°F. The mould temperature is maintained at 390°F for 2.5 minutes to
maintain the dispersion at or above the curing temperature, after which the mould
temperature is lowered rapidly to ambient temperature. The colour of the device is
brownish bronze. A strong medicinal odour emanating from the finished resin is
detected.

Analysis of the device after curing and cooling shows the naled content of the device to be 26% by weight.

The polyvinyl chloride dispersion used is commercially available from the Diamond Shamrock Company, U.S.A. (as PVC 7502) and is a high molecular weight homopolymer dispersion resin having a particle size less than two microns; specific viscosity is 1.62 to 1.68 as measured in 1% solution of the resin in cyclohexane at 30°C according to ASTM procedure.

DOP is a plasticizer for PVC and EPO is a stabilizer. The "Bentone" is added to control the viscosity of the plastisol.

The above dispersion and extender resins are as easy to work with in producing a satisfactory device as any that have been used. However, as those skilled in this art well know, a large number of other materials, as discussed above, can be used. Naled is not known to react chemically with any synthetic resin, and considerable variations in both ingredients and proportions can be successfully used.

Example II.

The quantities and procedures of Example I are repeated except that an open-faced mould is utilized. The top side of the device is rounded due to the meniscus formed on filling the mould, the shape being retained during curing. The resulting device is brownish bronze and contains 25% naled. Apparently a small portion of the naled was lost by vaporization or by being carried off by vaporization of the surface porosity control component during curing. The same medicinal odour was present.

Example III.

The procedure of Example I is repeated using a plastisol dispersion consisting in parts by weight of:

- 20 PVC homopolymer dispersion resin
- 10 PVC homopolymer extender resin
- 18 di-2-ethylhexylphthalate (DOP)
- 2 epoxidized octyl tallate
- 22 naled (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate)
- 2 surface porosity control component (e.g., bromodichloroacetaldehyde)
- 25 amorphous silica particles, average particle size — 2.35 microns
- 1 stearic acid

A bronze coloured resin body suitable as a pest strip is obtained which analyzed 22% by weight of naled after curing and cooling. A medicinal odour was present.

Example IV.

Following the procedure of Example I and using a plastisol dispersion consisting in parts by weight of

- 20 PVC homopolymer dispersion resin
- 11 PVC homopolymer extender resin
- 9 di-2-ethylhexylphthalate (DOP)
- 2.5 epoxidized octyl tallate
- 1 bentone
- 28 naled (1,2-dibromo 2,2-dichloroethyl dimethyl phosphate)
- 2 surface porosity control component (e.g., bromodichloroacetaldehyde)
- 25 amorphous silica particles, average particle size — 2.35 microns
- 1.5 palmitic acid

a bronze coloured resin body suitable for use as a pest strip is obtained after curing and cooling which analyzed 26 weight percent naled after curing and cooling. A medicinal odour was present.

Example V.

The mixture and procedure of Example I is repeated except that 30 weight percent of a technical grade of naled (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate) commercially available from the Chevron Chemical Company, U.S.A., is used. This product is known to contain certain impurities such as bromodichloroacetaldehyde, chloral, carbon tetrachloride and various forms of

phosphates. These impurities constitute about 9 weight percent of the product and in large part are sufficiently volatile as to be released during the curing of the device or shortly thereafter and hence not to interfere with the functioning of the device.

The device formed and cured in the manner indicated in Example I is brownish bronze and contains about 26 weight percent naled.

Example VI.

A uniform mixture (in parts by weight) is made of

29.0 p.b.w. polyvinyl chloride homopolymer general purpose resin	10
15.3 p.b.w. di-2-ethylhexyl phthalate (DOP)	10
2.0 p.b.w. epoxidized octyl tallate (EPO)	
25.7 p.b.w. naled (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate)	
3.0 p.b.w. bromodichloroacetaldehyde	
20.0 p.b.w. amorphous silica particles, average particle size 2.35 microns	15
1.0 p.b.w. stearic acid	
4.0 p.b.w. heat-stabilizer and lubricant	

The heat stabilizer and lubricant is a mixture of 3.3 p.b.w. dibasic lead phosphate and 0.7 p.b.w. dibasic lead stearate. The mixture is fed to an injection moulding machine and injection moulded into the shape shown in the Figure at a temperature of 265°F and a pressure of from 10,000 to 22,000 psi. The colour of the device is brownish bronze and a strong medicinal odour emanating from the moulded device is detected.

Analysis of the device after cooling shows the naled content to be about 25% by weight.

Naled Release Rates

The release rate of naled from compositions utilizable in this invention for a given surface area of a device of a given thickness and surface area varies depending upon not only the initial naled concentration, but more importantly on whether or not the volatile additive which serves as a porosity control component has been used as discussed above.

One significant advantage of the naled device of the present invention over the prior art DDVP device in current commercial use is found in the pattern of release of insecticide as a gas during the first few days of activation which starts at the moment of removal from a sealed container. The initial release rate of naled during the first few days is only a fraction of the initial release rate of DDVP from comparable devices due mainly to the difference in vapour pressure. For naled with porosity control additive, the release rate does not decrease noticeably for a period of about 10 weeks; thereafter, the release rate gradually decreases to about 50% of the maximum at the end of about 20 weeks. The pattern of the release rate curve for naled from a PVC device without the porosity control component is generally parallel. However, the total amount of naled released from a device made from a formulation containing the porosity control component is significantly higher (e.g., 10% or more) than that released from a device made from a similar formulation without the porosity control component which indicates that more naled is being released at any given time within that 20 week period for the former device than the latter device.

Comparative Example A.

Following the procedure of Example II and using a plastisol dispersion consisting in parts by weight of

20 PVC homopolymer dispersion resin	50
12 PVC homopolymer extender resin	
15 di-2-ethylhexylphthalate	
2 epoxidized octyl tallate	
30 naled (1,2-dibromo-2,2-dichloroethyl dimethyl phosphate)	
20 amorphous silica particles, average particle size — 2.35 microns	55
1 stearic acid	

a curved strip was produced. The cured strip contains about 25% weight naled

indicating that more of the naled initially present in this dispersion was lost during the curing process than that lost in Example II.

Example VII.

- 5 The procedure and quantity of Example I is repeated. The resulting device having a 1 square inch surface area is designated "A". Similar devices are made according to the procedure and quantity of Example I except that 1% (by weight) stearic acid is utilized in place of the palmitic acid (device "B"), 2% (by weight) stearic acid is utilized in place of the palmitic acid (device "C"), the palmitic acid component is omitted (device "D"), the silica component is omitted (device "E") and both the silica and palmitic acid components are omitted (device "F").
- 10 Each of these devices is suspended in a 20 cubic foot cell having dimensions of 2' x 2' x 5'. The cells consisted of a framework covered on the end and three sides with a kraft-paper-foil laminate, closed on the top with plate glass to facilitate observation. The strips are suspended from the top in the middle of the cell so as not to touch the sides or bottom of the cell. The test is conducted for 16 weeks.
- 15 Visual observations of the surfaces of each device are made daily to determine the formation of liquid droplets of naled. The observations include the time at which the surface first appears "slick" or "wet" with bead or droplet formation, the first time at which run marks are observed and the time at which drops are actually formed on the bottom of the sample. These results are shown below in Table I.
- 20

TABLE I

Time for onset of:	Device					
	A	B	C	D	E	F
First real "slick" look showing up-(no "beading")	7- 8 wks	10 wks	10 wks	4- 5 wks	2 wks	2 wks
Actual "beading" noticeable	12-13 wks	15-16 wks	15-16 wks	6 wks	4 wks	4 wks
Runs marks observable no dripping yet				7- 8 wks		
Actual drop formation at bottom of sample				10 wks		

15

As may be seen from the Table, the devices which did not contain both the silica component and the C₁₄ to C₂₀ saturated aliphatic carboxylic acid component exhibit beading in relatively short times. Both Device E (acid but no silica) and Device F (which contained neither silica nor the acid) show a slick look in about 2 weeks and beading in about 4 weeks while Device D (silica but no acid) shows beading in about 6 weeks and drop formation in about 10 weeks. All of the devices of the present invention (Devices A, B and C) show beading at a considerably later time and no drop formation.

The biological activity of Devices B, C and D is measured against SRS (Standard Reference Strain) susceptible *Musca domestica*.

25 of the SRS susceptible houseflies are added each day to each cell containing a device. The LT₅₀ value (in minutes) is measured. As known in the art LT₅₀ is the time for lethal effect on 50% of the insects introduced. Table II shows the values obtained for male SRS Susceptible houseflies. Similar results are obtained also with female SRS Susceptible houseflies although the latter are generally more resistant.

TABLE II

LT₅₀ - Minutes SRS Susceptible - LT₅₀, minutes

Age of Device - Days	B	C	D
1	50	51	48
2	45	44	47
13	55	54	55
14	55	61	59
21	53	-	54
23	-	66	-
29	-	57	-
30	-	54	62
34	-	79	69
37	48	-	-
49	68	-	62
50	76	-	66
51	-	77	-
55	86	83	81

The values obtained indicate that the addition of the acid component does not affect the biological activity of the devices. Similar results are obtained when the tests are repeated with CSMA (NAIDM) Susceptible *Musca domestica* and resistant strains FC, Orlando DDT and Isolan-B *Musca domestica*; the latter are pure, resistant strains of *Musca domestica* (see Bull, World Health Organ., Vol. 52, 1975, pages 101-108).

Example VIII.

Tests of biological activity on houseflies (*Musca domestica*), both resistant and susceptible strains and mosquitos (*Culex pipiens*) are conducted in the cell utilized in Example VII. The insects are introduced into the cell containing a device made

in accordance with Example I and containing 25% by weight naled. Both the LT_{50} and LT_{95} are measured. The results are shown below in Table III.

TABLE III
LT, minutes (70°F)

Age, Device (days)	Resistant Flies		Susceptible Flies		Culex pipiens	
	LT_{50}	LT_{95}	LT_{50}	LT_{95}	LT_{50}	LT_{95}
1			38 ^x	90 ^x	34	60
3	34 ^x	89 ^x				
28			92	198	71	89
30	78	129				
56			95	244	73	112
59	112	178				
84			110	208	104	146
87	30 ^{xx}	184 ^{xx}				
112			144	262	73	114
115	149	314				
140			143	317	83	116
143	107	286				

^x Flies apparently weak

^{xx} Some flies of low viability

The results show that the naled-containing devices emitted the naled insecticide slowly and uniformly over a 20 week period. The devices were effective in killing both resistant and susceptible houseflies as well as the less hardy mosquitoes. Similar tests conducted with *Drosophila melanogaster* show that these insects are also killed faster than houseflies.

Similar devices containing 25 weight percent naled are hung in the hallway of a building for 20 weeks and exposed to ambient temperatures. The percent naled remaining in the devices (average of 5 devices) is shown in Table IV.

TABLE IV

Exposure Time (Weeks)	Wt. % Naled Remaining in Exposed Devices
0	25.25
1	24.66
2	23.22
4	21.22
8	17.38
12	15.98
16	13.28
20	12.34

This test further shows that the devices release the naled insecticide uniformly over a prolonged period of time. Although some beading of the naled insecticide is noticed at about 16 weeks exposure, no drops or run marks are observed at the end of the 20 week test.

Example IX.

Samples of various household surfaces (aluminium foil, synthetic fibre carpet, particle board, wood, wood-semi-gloss enamel, vinyl wallpaper, wood-gloss enamel, vinyl flooring and tempered hardboard) are placed in a cell as utilized in Example VII and exposed for 102 days to the 25.7 weight percent naled-containing device of Example VI. The devices are utilized in an amount of one device per 20 cubic feet (Run G) and two devices per 20 cubic feet (Run H). Identical samples are exposed for the same time to a commercially available pest strip containing 20% by weight DDVP (dimethyl 2,2-di-chlorovinyl phosphate) at a rate of one device per 20 cubic feet (Run I). The adsorption of the naled or DDVP toxicant was determined by biological activity of the exposed material placed in a sealed one U.S. gallon tank in which houseflies are introduced. The LT_{50} values for each is measured and the time in days for each to reach an LT_{50} of 300 minutes by ventilation of the tank is estimated. The results are shown below in Table V.

TABLE V

	LT_{50} - Minutes			Estimated Days Ventilation To Reach LT_{50} 300 Min.		
	G	H	I	G	H	I
Aluminium Foil	No Effect	No Effect	No Effect	-	-	-
Carpet-Synthetic Fibre	185	125	40	>1 <5	>1 <5	13
Particle Board - Vinyl	135	86	37	6	12	16
Wood	104	76	38	5	15	20
Wood Semi-Gloss Enamel	125	109	50	9	12	28
Wall paper - Vinyl	110	78	34	11	13	36
Wood - Gloss Enamel	125	79	40	24	30	40
Vinyl Flooring	128	98	35	9	13	42
Tempered Hardboard	135	102	50	7	15	46

The results show that considerably less naled is adsorbed on the surfaces than DDVP (as evidence by the much longer LT_{50} times for naled). With ventilation, the naled was desorbed much faster than the DDVP. Similar tests are performed with various foods (potato, apple, bread, lettuce, tomato, orange and hamburger) with 24 hour exposure. DDVP adsorption (as compared with naled) was even higher. DDVP is adsorbed on all foods tests with LT_{50} values ranging from 12 minutes (potato) to 51 minutes (hamburger). Naled at the same concentration is not adsorbed on a number of the foods tested and when adsorbed, exhibits LT_{50} values ranging from 155 minutes (potato) to 380 minutes (sliced apple).

Comparative Example B.

An investigation is undertaken to determine the effects of various materials on the release rates and efficacy of polyvinyl chloride formulations containing about 25 weight percent naled, about 3 weight percent of a porosity control component and minor amounts of PVC plasticizers and stabilizers.

On the basis of an initial screening, calcium carbonate, aluminium oxide and various silicone fluids and resins are found to be unsuitable either because of their reactivity with naled or the porosity control component or because of strong incompatibility with the PVC formulations, even at relatively low loading levels of about 5 to 15 weight percent in the formulation. Several grades of powdered polyethylene and ethylene-vinyl acetate resins are also tested and determined unsuitable due to their extremely high plasticizer absorption as well as their cost.

Several grades of solid glass microspheres (average particle sizes ranging from about 6 to 50 microns) are also tested. All grades of solid glass microspheres exhibit relatively bad settling problems (greater with increasing particle size). In addition, devices made in accordance with Example 1 containing 25 weight percent naled and 45 weight percent of the solid glass microspheres exhibit a surface slickness (or sweating) after only 2 to 3 weeks. Similar samples made including 45 weight percent silica particles (in one instance, all particles through a 325 mesh sieve 95% of the particles less than 40 microns and in another instance, all through a 200 mesh sieve, 95% less than 75 microns) exhibit sweating in 5 to 6 weeks.

Summary of Advantages

The insect-combating device of the present invention contains relatively high amounts of naled which are uniformly released over a prolonged period of time. Naled has a reduced toxicity as compared to the prior art DDVP-containing devices and shows a substantially lower tendency towards adsorption on surfaces near the device.

Even though naled has been known and commercially available for a number of years prior to the present invention, and considerable research has been done with the use of naled as an insecticide, its substitution for DDVP in an insect-combating device has not been considered feasible. Efforts to shape a pet collar containing naled as the insecticide were unsuccessful in the initial research, so that actual testing of the effectiveness of naled for controlling fleas was made quite difficult. In addition, naled was not considered to be a likely candidate as a substitute for DDVP since its vapour pressure is known to be less than 2% of the vapour pressure of DDVP. Moreover, the problem of spewing with naled concentrations above about 25% set upper limits on the amount of naled that can be used in an article. The device of the present invention containing the spew-retarding amounts of finely divided silica and at least one C_{14} to C_{20} saturated aliphatic carboxylic acid or salt or ester thereof allows the use of naled even above 25% without spew formation on the device.

By including volatile additives in the mixture used in forming the device, it has been possible to increase the naled release rate to a level which allows for the mass production of a suitable insect-combating device.

The device in accordance with the present invention is produced to have a porous outer surface to not only release naled at a rate higher than otherwise possible and in a greater gross amount, but also to release naled at a rate effective to control insects for a substantially longer period than otherwise possible.

WHAT WE CLAIM IS:—

1. A device for combating insects comprising a shaped solid body constituted by a solidified mixture which has been shaped at elevated temperature of a synthetic resinous matrix material, from 15 to 35 weight percent of naled, a minor amount effective to retard spewing of the naled of finely divided silica particles and of at least one C_{14} to C_{20} saturated aliphatic carboxylic acid or a salt or ester thereof, and a surface porosity control component that is non-reactive in the mixture and has a boiling point at or below the shaping temperature to produce surface openings in communication with pores in the body by vaporization of the porosity control component to provide for release of naled gas at a rate effective to combat insects in the vicinity of the body but insufficient to form as spew on the body.

2. A device as claimed in Claim 1 wherein the silica particles are present in an amount in the range from 10 to 35 weight percent of the body and the acid or salt or ester is present in an amount in the range from 0.25 to 3 weight percent of the body.

3. A device as claimed in Claim 1 or Claim 2 wherein the synthetic resinous matrix material is a polyvinyl chloride.

4. A device as claimed in any of the preceding Claims wherein the mixture contains a minor proportion of a surface porosity control component having boiling point in the range from 170°F to 400°F.

5. A device as claimed in any of the preceding Claims wherein the surface porosity control component is selected from chloroacetaldehyde, dichloroacetaldehyde, chloral, bromoacetaldehyde, dibromoacetaldehyde, bromal, bromodichloroacetaldehyde, chlorodibromoacetaldehyde, bromochloroacetaldehyde, 2-bromopropanol and mixtures thereof.

6. A device as claimed in any of the preceding Claims the body of which has a regular symmetrical matrix of cavities which extend through the body, the cavities



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Several grades of solid glass microspheres (average particle sizes ranging from about 6 to 50 microns) are also tested. All grades of solid glass microspheres exhibit relatively bad settling problems (greater with increasing particle size). In addition, devices made in accordance with Example I containing 25 weight percent naled and 45 weight percent of the solid glass microspheres exhibit a surface slickness (or sweating) after only 2 to 3 weeks. Similar samples made including 45 weight percent silica particles (in one instance, all particles through a 325 mesh sieve 95% of the particles less than 40 microns and in another instance, all through a 200 mesh sieve, 95% less than 75 microns) exhibit sweating in 5 to 6 weeks.

Summary of Advantages

The insect-combating device of the present invention contains relatively high amounts of naled which are uniformly released over a prolonged period of time. Naled has a reduced toxicity as compared to the prior art DDVP-containing devices and shows a substantially lower tendency towards adsorption on surfaces near the device.

Even though naled has been known and commercially available for a number of years prior to the present invention, and considerable research has been done with the use of naled as an insecticide, its substitution for DDVP in an insect-combating device has not been considered feasible. Efforts to shape a pet collar containing naled as the insecticide were unsuccessful in the initial research, so that actual testing of the effectiveness of naled for controlling fleas was made quite difficult. In addition, naled was not considered to be a likely candidate as a substitute for DDVP since its vapour pressure is known to be less than 2% of the vapour pressure of DDVP. Moreover, the problem of spewing with naled concentrations above about 25% set upper limits on the amount of naled that can be used in an article. The device of the present invention containing the spew-retarding amounts of finely divided silica and at least one C_{14} to C_{20} saturated aliphatic carboxylic acid or salt or ester thereof allows the use of naled even above 25% without spew formation on the device.

By including volatile additives in the mixture used in forming the device, it has been possible to increase the naled release rate to a level which allows for the mass production of a suitable insect-combating device.

The device in accordance with the present invention is produced to have a porous outer surface to not only release naled at a rate higher than otherwise possible and in a greater gross amount, but also to release naled at a rate effective to control insects for a substantially longer period than otherwise possible.

WHAT WE CLAIM IS:—

1. A device for combating insects comprising a shaped solid body constituted by a solidified mixture which has been shaped at elevated temperature of a synthetic resinous matrix material, from 15 to 35 weight percent of naled, a minor amount effective to retard spewing of the naled of finely divided silica particles and of at least one C_{14} to C_{20} saturated aliphatic carboxylic acid or a salt or ester thereof, and a surface porosity control component that is non-reactive in the mixture and has a boiling point at or below the shaping temperature to produce surface openings in communication with pores in the body by vaporization of the porosity control component to provide for release of naled gas at a rate effective to combat insects in the vicinity of the body but insufficient to form as spew on the body.

2. A device as claimed in Claim 1 wherein the silica particles are present in an amount in the range from 10 to 35 weight percent of the body and the acid or salt or ester is present in an amount in the range from 0.25 to 3 weight percent of the body.

3. A device as claimed in Claim 1 or Claim 2 wherein the synthetic resinous matrix material is a polyvinyl chloride.

4. A device as claimed in any of the preceding Claims wherein the mixture contains a minor proportion of a surface porosity control component having boiling point in the range from 170°F to 400°F.

5. A device as claimed in any of the preceding Claims wherein the surface porosity control component is selected from chloroacetaldehyde, dichloroacetaldehyde, chloral, bromoacetaldehyde, dibromoacetaldehyde, bromal, bromodichloroacetaldehyde, chlorodibromoacetaldehyde, bromochloroacetaldehyde, 2-bromopropanol and mixtures thereof.

6. A device as claimed in any of the preceding Claims the body of which has a regular symmetrical matrix of cavities which extend through the body, the cavities



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having substantially parallel axes that intersect at least one substantially straight line along one dimension of the body.

7. A device as claimed in any of the preceding Claims the body of which is flexible and contains from 20 to 30 weight percent naled, from 15 to 25 weight percent of finely divided silica particles, from 0.5 to 1.5 weight percent of the acid or salt or ester, and from 1 to 3 weight percent of the surface porosity control component.

8. A device as claimed in Claim 7 wherein the synthetic resin is a polyvinyl chloride resin, the finely divided silica particles are all below 200 mesh size and at least 90% by weight thereof have a particle size of less than 75 microns, the acid is palmitic or stearic acid, and the polyvinyl chloride resin has been formed into the said body from a liquid plastisol dispersion including the surface porosity control component by filling a casting mould pre-heated to a temperature of about 290°F which is thereafter increased to about 360°F, the body being thereafter cooled and removed from the mould.

9. A device as claimed in Claim 8 the body of which has been formed by increasing the mould temperature from about 290°F to about 360°F in a hot air, radiant heated oven for about two minutes.

10. A device as claimed in Claim 8 or Claim 9 the body of which has been formed by injection moulding of the mixture.

11. A device as claimed in Claim 1, substantially as described in any of the Examples.

12. A method of combating insects which comprises placing and maintaining a device as claimed in any of the preceding claims in an area in which insects are to be combated.

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