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(54) Title: INSECTICIDAL MICROCRYSTALLINE DRY AEROSOL SPRAY

(57) Abstract: An insecticidal formulation which provides excellent secondary insect kill is disclosed herein. The insecticidal formulation comprises deltamethrin volatile solvents such as octane, propellants such as fluorinated hydrocarbons. The solvents and propellants must flash off at room temperature when sprayed to result in microcrystals of the deltamethrin being deposited on the target surface.

INSECTICIDAL MICROCRYSTALLINE DRY AEROSOL SPRAY

Background and Summary of the Invention:

This invention relates to a novel insecticidal formulation that forms microcrystalline insecticide when the formulation is sprayed. Using the formulation of this invention crystals form rapidly, precipitating insecticide before it has a chance to absorb into porous surfaces, as in the case of conventional formulations delivered as an aerosol. The formulation of this invention has the additional benefit that the microcrystals are easily picked up from a surface by the insects, particularly targeted are cockroaches and ants, who then transfer the active formulation to other cockroaches and ants. This provides the formulation the advantageous property of what is known in the art as secondary kill. By secondary kill a cockroach that has not been directly exposed to the insecticide is killed either by contact to exposed cockroaches or to surfaces upon which exposed insects have deposited the insecticide.

It is extremely desirable for a product to have good residual performance and secondary kill. This is because the roaches are most active at night, hence this novel formulation will be available for the cockroaches when they are most active. With favorable secondary kill properties an insecticide in a preferred formulation, such as in the instant formulation, the insects, themselves, will spread the active formulation to their habitat.

Conventional insecticide products rely on the user to spray or apply the formulation containing the active insecticidal ingredient directly onto the insects or to the habitat of the insect. Since cockroaches are nocturnal, direct application will not be practical or effective unless the user is present when the cockroaches are present. Though many insecticide products claim residual control, those claims are based on long periods of forced exposure of the insects to the surface, *i.e.,* 24 hours of continuous exposure is common in the art. This extended exposure time is required to kill the roaches, because the insecticide must be absorbed by the roach from the surface where the active has been applied. With the formulation of the present invention long exposure time is not necessary, because the crystals sit on the surface, are readily accessible to the insect and can be easily picked up within a few minutes.

Conventional aerosol insecticides, either water or oil based, contain solvents in which the insecticide is dissolved. Typically, the solvent is based on mixtures of normal paraffins. These paraffins not only dissolve the insecticide, they also facilitate wetting the insect when it is sprayed directly with the product. This allows for faster transfer and uptake of the insecticide by the insect, and provides what is known in the art as "knockdown." However, due to EPA regulations formulators use paraffins that are long chain hydrocarbons (typically C-14 and longer), so they are not considered by the EPA to be volatile organic compounds (VOC's). Hence, the insecticide is dissolved in a solvent having low volatility. When such a product is dispensed on a porous surface, the solvent seeps into the surface carrying the insecticide with it. This drastically diminishes the residual performance of the product because it is no longer available on the surface for the insect.

Secondary kill is not possible for conventional aerosol insecticides because an insect cannot pick up a sufficient quantity of insecticide to kill other insects that have not been exposed to the treated surface. On non-porous surfaces like tile, conventional aerosol insecticide products that are solid at room temperature, *e.g.* Baygon or Dursban (O,O-diethyl O-3,5,6-triehloro-2-pyridinyl phosphorothioate) will form crystals on the surface. However, because the insecticide evaporates so slowly (over hours or days) the subsequent crystals are very large (on the order of millimeters) which do not exhibit secondary kill. With the volatile solvents used in the present formulation (combinations of one or more of the following: propane, heptane, octane short chain alcohols (C_1-C_8), and dymel (1,1 difluoroethane) (152a)) the solvent evaporates within seconds, which not only keeps the insecticide from adsorbing on the surface but also causes small crystals to form (on the order of 30 microns). Excellent secondary kill is exhibited by this novel insecticidal formulation.

Conventional insecticides often exhibit what is known in the art as repellence. This is the behavior of the insects to avoid treated surfaces. Often this repellence has been observed to come from an irritating but non-lethal contact between the roach and the surface. After that the roach will not return to the surface. It is therefore necessary that the roach pick-up the insecticide on its first contact. Because the insecticide in this formulation is easily picked up by the roaches, the roach will die in its first contact.

One method known to the art for keeping insecticides on the surface so that it is accessible for pick-up by the roaches is microencapsulation. This is a process in which small spheres of insecticide are formed in which the insecticide is trapped within a polymer coating. This system is unstable in systems containing oil because the insecticide can diffuse through the membrane if there is a driving force for diffusion. If the microcapsule contacts a lipophobe in which the insecticide is soluble it will diffuse out from the microcapsule. Because aerosols contain either hydrophobe solvents or propellants, it is extremely difficult to formulate a product that will exhibit even short-term stability. One way of doing this is to make an emulsion, which isolates the microcapsules from the hydrophobe phases. However, the method for preparing such emulsions is difficult and if there is a mistake in manufacturing, the microcapsules may end up in the oil phase, releasing the insecticide. If this insecticide is irritating or toxic at a sufficient dosage or rate this instability of the microcapsule may pose a consumer health risk.

The micro crystal formulation of the instant invention delivers the benefits of microencapsulation without the challenges and risks associated with such a formulation. Additionally, it uses a high level of propellant (>80%) which is not known to the art how to formulate using microcapsules. This high level of propellant allows the formation of very small aerosol particles (<30 microns) which can diffuse into hard to reach places where roaches hide. Again, this is advantageous because the roaches are not active during the daylight hours and the products' ability to diffuse back to where the roaches harboarage is extremely advantageous for the consumer. The present formulation also delivers the consumer desirable benefits of no mess (no solvent) and no odor (no solvent).

Detailed Description of the Invention:

The present invention employs a unique system of solvent and propellant which enhances the delivery and effectiveness of the active ingredient. A propellant or propellant/solvent mixture and insecticide(s) combination is selected, such that the insecticide(s) is soluble in the propellant or propellant/solvent mixture, and the insecticide will be a solid phase once the propellant or propellant/solvent has flashed off, or the insecticide is present in a viscous suspension of powdered insecticide in a formulation in which it is not soluble.

Typical pesticides useful in this invention include:

Deltamethrin	(S)-α -cyano-3-phenoxzybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate
Baygon	2-(1-methylethoxy)phenyl methylcarbamate (CAS)
Tetramethrin	N-(chrysantemoxymethyl)-1-cyclohexene-1,2-Dicarboximide
Bifenthrin	[1α.3α(Z)] (=)-(2 methyl[1,1'-biphenyl]-3-yl) methyl 3-(2-chloro-3,3,3- trifluro-1-propenyl)-2.2-dimethylcyclopropanecarboxylate (CAS)

This formulation may include a corrosion inhibitor common to the art e.g. sodium benzoate, nitromethane, thioacetamide, 2-mercaptobenzimidazole, etc.

Surfactant systems common to the art could be used to form this water in oil emulsion, such as nonyl phenol ethoxylates, alkylbenzene sulfanates, sulfosuccinates, linear alkyl ethoxylates, polyethylene glycol esters, and the like.

Propellants useful in this invention are fluorinated propellants like dymel 152a such as a low boiling liquified gases such as butane, propane, dimethylether (DME) or blends thereof.

In the U.S. the use of volitile organic compounds (VOC) limit formulators to using less then 20% VOC materials. Hence, it would be possible to blend in less then 20% pentane, DME, or the like, with the dymel (152a). Internationally, any propellant that will dissolve the insecticide could be used, such as butane, propane, pentane, and the like. When nitrogen, CO2 or other compressed inert gasses are used--however this would require that the solvent for the insecticide be very volitile e.g. acetone, so that it would flash off within seconds and leave the crystalline active as described above.

The insecticide(s), solvent(s) are added to the empty aerosol container, it is then crimped and the propellant(s) are added. Typical formulations will contain >95% propellant/volatile solvent and the remainder insecticide. When this product is sprayed all of the propellant/volatile solvent flashes off, leaving a residue of the solid phase insecticide behind.

A preferred formulation that has been found to be particularly effective is 0.1-0.01%

deltamethrin dissolved in a blend of 1-10% n-octane and the bulk dymel 152a, (1,1 difluoroethane).

The above formulation will deliver the desired secondary kill and demonstrates easy pick up from the surface by the target insect. However, other materials may be added to provide additional benefits. Such additions considered are as follows:

Adjuvant such as silicone oils, *e.g.* dimethylsiloxane polymers; polymeric materials, surfactants, sugars, paraffins, ***etc.*** to increase pick up by the insect or to decrease the adhesion between the insecticide particles and the surface or slow the release of the insecticide;

Attractants such as fenugreek to bring insects into contact with the surface and/or increase the amount of contact time between insect and the surface.

Insect growth regulators may also be added;

Other insecticides can be added at low enough levels not to solvate the solid form insecticide, such as S-biolallethrin, prallethrin, tetramethrine, *and the like* , to speed up the knock-down of the formulation. For example deltamethrin is 15% soluble in S-biolallethrin, hence if deltamethrin is used at 0.03% the rate of S-biolallethrin must be less than 0.2% for the crystals to form, assuming there are no other low vapor pressure solvents in the formulation;

Solvents may also be added to deliver knock-down insecticide(s) more rapidly to the insect, further speeding up the knock-down. However these solvents must be volatile enough that the solvent will evaporate before having time to absorb into porous surfaces.

Fragrances, pigments, or other additives may also be employed depending on the particular use. These are well known in the art; and.

Trace amounts of anti-irritants may be added, such as esterol, to decrease the product irritance.

In accordance with this invention, the crystal size is important. In the development of this product solvents of different volatility were added to the formula and scanning electron (SEM) micrographs were taken of the resulting forms of the insecticide -deltamethrin. It was found that crystal size was inversely proportionate to the volatility of the solvent. The secondary kill efficacy was dependent on the form of the deltamethrin. When the crystals were small (1-50 microns) there was good secondary kill. However, with the less volatile solvents (*e.g.* peanut oil) huge crystals (> 100 microns) were formed with little or no secondary kill. Other solvents, like cyclohexanone, formed a sheet-like structure that had virtually no secondary kill.

One formulation to exhibiting particularly good performance is 0.04% deltamethrin, 0.01-0.3% S-biolallethrin, 0.5% octane, and bulk dymel 152A(1,1 difluoroethane).

Example 1

Insecticide formulations were tested for their ability to be picked up from a treated surface by cockroaches (primary) and be transferred to other cockroaches (secondary), resulting in the death of both the primary and secondary roaches.

Sample preparation: 6"x6" unfinished pine tiles were sprayed at a distance of 12" with different aerosol formulations for approximately 3 seconds. The aerosol was moved back and forth to insure that the entire tile has an even coating of the product. Each sample was labeled with its insecticide formulation treatment. Controls were similar in treated tiles.

The samples are allowed to sit overnight before being used.

Test Procedure:

1.) For each replicate/treatment 15 adult male german cockroaches (hmr Blatella germanica) are placed inside a 16 oz wide mouth glass jar with the sides greased with a mixture of white petrolatum and mineral oil (50:50).

2.) For each replicate/treatment 5 adult male german cockroaches (hmr Blatella germanica) are placed inside a plastic pint sized container with the sides greased with a mixture of white petrolatum and mineral oil (50:50).

3.) The pint container instep 2 in inverted and placed on top of the test surface, insuring that all roaches are on the surface for 5 minutes.

4.) Controls were used composed of jars with roaches exposed to untreated surfaces.

5.) After the 5 minutes the roaches are transferred in the glass jars of step 1, where they are in contact with the 15 uncontaminated roaches.

6.) The jars are left undisturbed for 24 hours, at which point the number of dead and live roaches are counted.

7.) The secondary kill is measured by taking the total number of roaches (20) and subtracting the roaches exposed to the surface (5) from the number of dead roaches and dividing this number by the number of roaches exposed to the surface, and multiplying by 100.

The results are reported as percent secondary kill

TABLE I

Sample ID	**Rep #**	**% 2ND Kill**
Foam 1	1	180
(0.04Δ)	2	120
	3	180
Raid Max	1	0
	2	0
	3	0
Black Flag	1	0
Gold	2	0
	3	0
Control	1	0
	2	0

Δ = deltamethrin

What is Claimed is:

1.) An insecticidal composition comprising deltamethrin, a solvent and a low boiling propellant.

2.) The composition of Claim 1 containing from about 0.01% to about 0.1% of deltamethrin, from about 1% to about 10% solvent and from about 98.99% to about 89.9% of propellant.

3.) An insecticidal composition comprising deltamethrin having a crystalline particle size of < 50 microns.

4.) The insecticidal composition of Claim 4 wherein the crystalline particle size is < 30 microns.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US01/29107

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :A01N 25/06
US CL :424/45
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/45

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,303,091 A(MAILANDER et al.) 07 February 1967, see entire document.	1-4
Y	US 4,826,674 A(ALBANESE) 02 May 1989, see entire document.	1-4

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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20 NOVEMBER 2001	14 JAN 2002

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