(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
10 September 2010 (10.09.2010)

PCT

(10) International Publication Number
WO 2010/101820 A1

(51) International Patent Classification:
A01N 25/02 (2006.01) *A01N 57/12* (2006.01)
A01N 25/28 (2006.01) *A01N 57/20* (2006.01)
A01N 57/16 (2006.01) *A01N 57/30* (2006.01)
A01N 57/28 (2006.01) *A01N 57/32* (2006.01)
A01N 57/14 (2006.01) *A01P 7/04* (2006.01)

(21) International Application Number:
PCT/US2010/025754

(22) International Filing Date:
1 March 2010 (01.03.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/157,297 4 March 2009 (04.03.2009) US

(71) Applicant *(for all designated States except US)*: **DOW AGROSCIENCES LLC** [US/US]; 9330 Zionsville Road, Indianapolis, IN 46268-1054 (US).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **WILSON, Stephen** [US/US]; 776 Sugarbush Drive, Zionsville, IN 46077 (US).

(74) Agent: **ARNETT, Charles**; 9330 Zionsville Rd, Indianapolis, Indiana 46268 (US).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

Published:

— *with international search report (Art. 21(3))*

WO 2010/101820 A1

(54) **Title**: MICROENCAPSULATED INSECTICIDE WITH ENHANCED RESIDUAL ACTIVITY

(57) **Abstract**: A method of formulating and using a microencapsulated insecticide with an extended field life after application of insecticidal activity. These methods include the steps of forming a microcapsule that includes at least one organophosphate insecticide and at least one non-volatile compound such as an esterified fatty acid that is at least partially surrounded by a polymer shell. These formulations can be used to control insect populations by singular or periodic applications of the microcapsule microencapsulated formulations to areas adjacent to insect populations.

MICROENCAPSULATED INSECTICIDE WITH ENHANCED RESIDUAL ACTIVITY

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Serial No. 61/157,197, filed March 4, 2009, which is expressly incorporated by reference herein.

FIELD OF THE INVENTION

[0002] Various aspects and embodiments relate generally to formulations of microencapsulated pesticides that exhibit advantageous biological, commercial and/or environmental properties including long effective periods of insecticidal activity after their application.

BACKGROUND

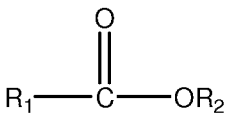
[0003] Controlling insect population is essential to modern agriculture, food storage and hygiene. Currently, encapsulated insecticidal formulations that are safe and effective play a significant role in controlling insect population. Properties of useful encapsulated insecticidal formulations include good efficacy against targeted pests, including good initial toxicity against targeted insects, ease of handling, stability, advantageous residence times in the environment and, in some instances, a long effective period of insecticidal activity after its application to an area adjacent to a population of insects.

[0004] Virtually all insecticidal formulations that lose their ability to kill or control insects must be reapplied resulting in increased material and labor costs. Additionally, formulations with a short period of post application activity can result in periods of time during which a surface adjacent to a population of insects is

vulnerable to infestation. There is a need then, for insect formulations that retain their activity for extended periods of time after their application. Various aspects and embodiment disclosed herein address the need for insecticidal formulations which retain their ability to kill or repel insects for an extended period of time after they have been applied to a surface adjacent to a population of insects.

SUMMARY

[0005] One embodiment of the invention is a method of formulating a microencapsulated insecticide in which the formulation retains its ability to kill or repel insects from a surface adjacent to a population of insects for at least 120 days after it is applied to the surface. One such method comprises the steps of: providing at least one insecticide, an esterified fatty acid, at least one monomer and a cross-linking agent; mixing the insecticide, the low volatility component and at least one monomer; and condensing the monomer to form a polymeric capsule shell that at least partially encapsulates a portion of the insecticide and a portion of the esterified fatty acid. In one embodiment the esterified fatty acid has Formula A, where A is:



wherein; R_1 is a straight chain or branched alkyl, or alkenyl group having from 11 to 25 carbon atoms, and

R_2 is a straight chain or branched alkyl, or alkenyl group having from 1 to 8 carbon atoms.

[0006] In one embodiment of the invention the ingredient in the formulation with insecticidal activity is an organophosphate insecticide. In one embodiment the organophosphate insecticide is selected from the group consisting of: acephate,

azinphos-methyl, chlorfenvinphos, chlorethoxyfos, chlorpyriphos, diazinon, dimethoate, disulfoton, ethoprophos, fenitrothion, fenthion, fenamiphos, fosthiazate, malathion, methamidophos, methidathion, omethoate, oxydemeton-methyl, parathion, parathion-methyl, phorate, phosmet, profenofos, and trichlorfon.

[0007] In still another embodiment the ingredient in the formulation that exhibits insecticidal activity is chlorpyrifos-methyl.

[0008] In one embodiment the formulation includes a microcapsule shell that at least partially encases an ingredient with insecticidal activity and is formed by an interfacial polycondensation of at least one monomer that is essentially insoluble in water and one monomer that is soluble in water. Oil soluble compounds that can be used to form the shell of the microcapsule may be selected from the group consisting of: diisocyanates, polyisocyanates, diacid chlorides, poly acid chlorides, sulfonyl chlorides, and chloroformates; water soluble monomer that can be used to form the shell can be selected from the group consisting of: diamines, polyamines, water soluble diols and water soluble polyols. In some embodiments the interfacial polycondensation step is carried out in the presence of a cross-linking agent such as an amine.

[0009] In one embodiment the esterified fatty acid in the formulation is methyl oleate.

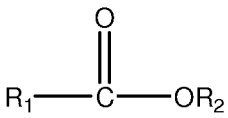
[0010] One embodiment includes forming a microcapsule having a shell thickness of between about 90 nm to about 150 nm. In still another embodiment the microcapsule shell has a thickness of about 100 nm to about 130 nm. In yet another embodiment the microcapsule shell has a thickness of about 120 nm.

[0011] Still another embodiment is a method for controlling an insect population, comprising the steps of: providing an insecticidal formulation that retains its ability to

kill or repel insects on a surface adjacent to a population of insects for at least 120 days and applying the formulation to a surface adjacent to an insect population. In still another embodiment the formulation retains its insecticidal activity or ability to repel insects for at least 150 days and in still another embodiment it retains its post application insecticidal activity for at least 170 days.

[0012] One embodiment is the method of controlling an insect population for an extended period of time following an application of the formulation, comprising the steps of providing an insecticidal formulation having a microcapsule shell or wall that at least partially surrounds a mixture including an insecticide and an esterified fatty acid (A), where:

A is:



wherein; R_1 is a straight chain or branched alkyl, or alkenyl group having from 11 to 25 carbon atoms, and

R_2 is a straight chain or branched alkyl, or alkenyl group having from 1 to 8 carbon atoms.

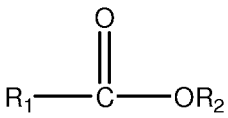
[0013] In some embodiment the insecticide is an organophosphate insecticide and the capsule is formed via an interfacial polycondensation of a water soluble and a water insoluble monomer polymer. Additional steps include, for example, applying the formulation to a surface adjacent to a population of insects.

[0014] In one embodiment the method of controlling an insect population includes a microencapsulated formulation that comprises an organophosphate insecticide. In one embodiment the organophosphate insecticide is selected from the group

consisting of: acephate, azinphos-methyl, chlorfenvinphos, chlorethoxyfos, chlorpyriphos, diazinon, dimethoate, disulfoton, ethoprophos, fenitrothion, fenthion, fenamiphos, fosthiazate, malathion, methamidophos, methidathion, omethoate, oxydemeton-methyl, parathion, parathion-methyl, phorate, phosmet, profenofos, and trichlorfon. In still another embodiment the organophosphate insecticide is chlorpyrifos-methyl.

[0015] In one embodiment the method of controlling an insect population includes the steps of applying a microencapsulated formulation of an insecticide in which the capsule wall is formed by an interfacial polycondensation between at least one oil soluble monomer selected from the group consisting of: diisocyanates, polyisocyanates, diacid chlorides, poly acid chlorides, sulfonyl chlorides, and chloroformates; and at least one water soluble monomer selected from the group consisting of: diamines, polyamines, water soluble diols and water soluble polyols and the polycondensation is carried out in the presence of an esterified fatty acid having Formula A, where:

A is:



wherein; R_1 is a straight chain or branched alkyl, or alkenyl group having from 11 to 25 carbon atoms, and

R_2 is a straight chain or branched alkyl, or alkenyl group having from 1 to 8 carbon atoms.

[0016] In one embodiment, the formulation includes between about 3 to about 30 wt. percent of the esterified fatty acid. Still another embodiment is a method of

controlling an insect population in an area adjacent to a population of insects for an extended period of time following an application of the insecticidal formulation, comprising the following steps: providing a microencapsulated insecticidal formulation that includes an esterified fatty acid according to Formula A in which the formulation continues to kill or repel insects for at least 120 days after its application. Yet another embodiment is a method for controlling an insect population in a given area that comprises the steps of: applying a microencapsulated insecticidal formulation in which the microcapsule has a shell thickness of between about 90 nm to about 150 nm and applying the microcapsule formulation to an area adjacent to a population of insects. In still another embodiment the microcapsule shell or wall has a thickness of about 120 nm.

[0017] In one embodiment the polymeric shell of the extended life insecticidal formulation is formed by cross-linking a water soluble monomer and a water insoluble monomer in the presence of amine such as diethylenetriamine, in the presence of an organophosphate insecticide and an esterified fatty acid.

[0018] Still another embodiment is an microencapsulated insecticidal formulation comprising, chlorpyrifos-methyl; methyl oleate; and a polymeric microcapsule shell, the shell comprising polyurea.

DETAILED DESCRIPTION

[0019] For the purposes of promoting an understanding of the principles of the novel technology, reference will now be made to the preferred embodiments thereof, and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the novel technology is thereby intended, such alterations, modifications, and further applications of the principles of

the novel technology being contemplated as would normally occur to one skilled in the art to which the novel technology relates.

[0020] As used herein, the terms "shell" and "wall" are used interchangabley with reference to microcapsules unless otherwise noted. These terms do not necessarily imply that a given shell or wall is completely uniform or that it completely encompasses whichever materials or components that are localized within the corresponding microcapsule.

[0021] The term "about" implies a range of values plus or minus 20 percent e.g. about 1.0 includes values from 0.8 to 1.2 and all values within this range.

[0022] The need to periodically apply various insecticidal formulations in order to control continuing pest infestations or to prevent their occurrence, increase the amount of insecticides that must be used and the cost associated with their shipping, handling and application. Unfortunately, most insecticides, especially liquid based preparations, lose their efficacy relatively soon after their application and must be re-applied to insure insect control. Accordingly, methods of formulating insecticides that increase their post application effective lifetime provide a significant benefit to those industries and individuals that rely on pesticides to control insect populations.

[0023] Methods for extending the post application activity span of insecticides include providing and applying powders or crystals of the active ingredients to areas adjacent to insect populations or to areas susceptible to insect infestation. Not all useful insecticides are amenable to these approaches and some very useful insecticides are most effective in a liquid or pseudo liquid form. Even when the compound is active in crystalline or powder form, there are some situations in which dry formulations have their own limitation, including an increased tendency for inadvertent dispersal by wind or rain or a tendency to fall to the ground and off

various elevated surfaces such as leaves, stems and flowering bodies where the compound is likely to exhibit its greatest utility. Another approach is to encapsulate the active ingredient in a formulation intended to somewhat protect the active ingredient from desiccation, dilution and/or unintended dispersal. Again, many of the currently available encapsulated formulations of various insecticides still loss activity relatively soon after their application to an area adjacent to a population of insects.

[0024] Various methods for formulating and using microencapsulated insecticidal formulations disclosed herein address this need by at least partially encapsulating the active insecticide in the formulation in a microcapsule along with a nonvolatile compound such as an esterified fatty acid. One group of insecticides that benefit from these types of formulations is the organophosphates. This class of insecticides includes, but is not limited to, acephate, azinphos-methyl, chlorfenvinphos, chlorethoxyfos, chlorpyriphos, diazinon, dimethoate, disulfoton, ethoprophos, fenitrothion, fenthion, fenamiphos, fosthiazate, malathion, methamidophos, methidathion, omethoate, oxydemeton-methyl, parathion, parathion-methyl, phorate, phosmet, profenofos, and trichlorfon. One especially useful organophosphate insecticide that benefits from being included in a microcapsule formulation that includes a nonvolatile component is chlorpyriphos-methyl.

[0025] As illustrated in Table 1, formulations of insecticides such as chlorpyrifos-methyl can be incorporated in microcapsules by forming the capsule in the presence of an inert liquid such as an esterified fatty acid, soybean oil, or polyglycol. Various formulations made either with or without methyl oleate were synthesized by methods presented in the experimental section.

[0026] Formulations of organophosphate insecticides, such as microencapsulated chlorpyrifos-methyl, generally lose their activity after their application.

Table 1

Compositions of representative formulations, based on the ingredients used to formulate the microcapsule.

Lot Number	A	B	C	D	E	F
Target capsule diameter (μm)	12	12	12	12	12	12
Target capsule wall thickness (nm)	120	80	120	80	120	120
Chlorpyrifos-methyl (g)	480	486.67	96.48	97.82	96.48	96.48
1-Nonanal (g)	9.6	9.73	1.93	1.96	1.93	1.93
Solvesso 150 (g)	470.4	476.93	94.55	95.86	94.55	94.55
Methyl Oleate (g)	-	-	95.04	96.36	-	-
Soybean Oil (g)	-	-	-	-	95.04	-
Polyglycol P-2000 (g)	-	-	-	-	-	95.04
PAPI 27 (g)	40.00	26.67	12.00	8.00	12.00	12.00
Diethylenetriamine (g)	10.99	-	3.30	-	3.30	3.30
Ethylenediamine (g)	-	6.40	-	1.92		
Gohsenol GL03 (g)	25.00	25.00	7.50	7.50	7.50	7.50
Veegum (g)	13.00	13.00	3.90	3.90	3.90	3.90
Kelzan S (g)	1.62	1.62	0.49	0.49	0.49	0.49
Atlox 4913 (g)	13.91	13.91	4.17	4.17	4.17	4.17
Water (g)	1087.48	1130.06	317.80	305.40	317.80	317.80
Measured capsule diameter (μm)	11.3	11.8	11.4	11.8	12.2	11.6

Key to trade names and abbreviations used in Table 1.

Solvesso 150- Xylene-range aromatic solvent, Exxon
Polyglycol P-2000- Poly(propylene glycol), Dow Chemical
PAPI 27- polymethylene polyphenylisocyanate, Dow Chemical
Gohsenol GL03- poly(vinyl alcohol), Nippon Gohsei
Veegum- bentonite clay, R. T. Vanderbilt
Kelzan S- xathan gum, Kelco
Atlox 4913- polymeric surfactant, Croda

[0027] Referring now to Table 2, the sizes of these microcapsules were measured and they were assigned a one letter code. Next, these formulations were

then applied to surfaces adjacent to insect populations, in order to measure their effectiveness.

TABLE 2

Chlorypyrifos-methyl microcapsules formulated with and without nonvolatile solvents.

Formulation ID.	Solvent(s)	Amine	Particle Size (VMD, µm)	Wall Thickness (nm)
A	Solvesso 150	DETA	12	120
B	Solvesso 150	EDA	12	80
C	methyl oleate, Solvesso 150	DETA	12	120
D	methyl oleate, Solvesso 150	EDA	12	80
E	soybean oil, Solvesso 150	DETA	12	120
H	soybean oil, Solvesso 150	EDA	12	80
F	polyglycol P-2000, Solvesso 150	DETA	12	120
I	polyglycol P-2000, Solvesso 150	EDA	12	80

A qualitative summary of some components of microcapsule formulations of insecticide formed with, and without, inert non-volatile components such as soybean oil, polyglycol, or esterified fatty acids.

Table 3

Application Data, including the dilution of the formulation made prior to its application and the application rate of the formulation used to test various formulations on various surfaces.

Formulation ID	Formulation g/l C-M	Amount of sample added to water ml	Application rate ml/m^2
A	240	4.17 in 45.83	50 ml
B	240	4.17 in 45.83	
C	150	6.67 in 43.33	
D	150	6.67 in 43.33	
E	150	6.67 in 43.33	
F	150	6.67 in 43.33	
G	750 g/kg	2.68 g made up to 50 ml	
Untreated control	-	-	

In order to test the efficacy of the microencapsulated formulations disclosed herein these formulations along with control formulations were applied to the following surfaces, gypsum, wood and mud. These formulations, along with control formulations, were monitored for their activity against a species of mosquito, *Anopheies arbaiensis*. These studies were carried-out over about a 170 day time period, data collected in these tests are presented in Tables 4-8, and summarized in Table 9.

Table 4

Mortality Results *Anopheles arabiensis*.

Period after treatment	Test surface	Sample code	Knockdown counts Out of 15					Mortality counts Out of 15				
			Replicates After 30 min.				Total out of 60	Replicates After 24 hours				Total Out of 60
			1	2	3	4		1	2	3	4	
1 day	Gypsum	A	2	4	3	1	10	15	15	15	15	60
		B	11	13	12	10	46	15	15	15	15	60
		C	4	9	7	9	29	15	15	15	15	60
		D	14	15	14	13	56	15	15	15	15	60
		E	4	5	3	6	18	15	15	15	15	60
		F	14	14	15	14	57	15	15	15	15	60
		G	12	13	11	16	51	15	15	15	15	60
		Control	-	-	-	-	-	1	0	0	3	4
	Wood	A	10	9	28	7	34	15	15	15	15	60
		B	12	13	11	15	51	15	15	15	15	60
		C	8	9	7	10	34	15	15	15	15	60
		D	12	13	13	14	52	15	15	15	15	60
		E	14	10	12	11	47	15	15	15	15	60
		F	15	14	15	15	59	15	15	15	15	60
		G	10	13	11	10	44	15	15	15	15	60
		Control	-	-	-	-	-	0	1	1	1	3
1 day	Mud	A	2	4	3	1	10	15	15	15	15	60
		B	11	13	12	10	46	15	15	15	15	60
		C	4	9	7	9	29	15	15	15	15	60
		D	14	16	14	13	56	15	15	15	15	60
		E	4	5	3	6	18	15	15	15	15	60
		F	14	14	15	14	57	15	15	15	15	60
		G	12	13	11	15	51	15	15	15	15	60
		Control	-	-	-	-	-	1	0	0	3	4

Mortality results measured against *Anopheles arabiensis,* determined 1 day after the application of the formulation to an area that includes the pest.

Table 5

Mortality Results *Anopheles arabiensis*.

Period after treatment	Test surface	Sample code	Knockdown counts Out of 15					Mortality counts Out of 15				
			Replicates After 30 min.				Total out of 60	Replicates After 24 hours				Total Out of 60
			1	2	3	4		1	2	3	4	
1 month	Gypsum	A	0	0	0	0	0	15	15	15	15	60
		B	0	0	0	0	0	15	15	15	15	60
		C	0	0	0	0	0	15	15	15	15	60
		D	2	0	3	1	6	15	15	15	15	60
		E	0	0	0	0	0	15	15	15	15	60
		F	0	0	0	0	0	15	15	15	15	60
		G	2	1	2	2	7	15	15	15	15	60
		Control	-	-	-	-	-	0	2	1	2	5
	Wood	A	0	0	0	0	0	15	15	15	15	60
		B	0	0	0	0	0	15	15	15	15	60
		C	0	0	0	0	0	15	15	15	15	60
		D	3	5	4	2	14	15	15	15	15	60
		E	0	0	0	0	0	15	15	15	15	60
		F	0	0	0	0	0	15	15	15	15	60
		G	0	0	0	0	0	15	15	15	15	60
		Control	-	-	-	-	-	1	1	1	3	6
1 month	Mud	A	0	0	0	0	0	13	15	7	9	44
		B	0	0	0	0	0	6	15	9	4	34
		C	0	0	0	0	0	15	6	15	15	51
		D	0	0	0	0	0	7	3	2	0	12
		E	0	0	0	0	0	6	13	15	12	46
		F	0	0	0	0	0	10	1	0	0	11
		G	0	0	0	0	0	15	14	12	15	56
		Control	-	-	-	-	-	0	0	1	2	3

Mortality results measured against *Anopheles arabiensis,* determined 1 month after the application of the formulation to an area that includes the pest.

Table 6

Mortality Results *Anopheles arabiensis*.

Period after treatment	Test surface	Sample code	Knockdown counts Out of 15					Mortality counts Out of 15				
			Replicates After 30 min.				Total out of 60	Replicates After 24 hours				Total Out of 60
			1	2	3	4		1	2	3	4	
2 months	Gypsum	A	0	0	0	0	0	15	15	15	15	60
		B	0	0	0	0	0	15	15	15	15	60
		C	0	0	0	0	0	15	15	15	15	60
		D	2	0	3	1	6	15	15	15	15	60
		E	0	0	0	0	0	15	15	15	15	60
		F	0	0	0	0	0	15	15	15	15	60
		G	2	1	2	2	7	15	15	15	15	60
		Control	-	-	-	-	-	1	0	1	1	3
	Wood	A	0	0	0	0	0	15	15	15	15	60
		B	0	0	0	0	0	15	15	15	15	60
		C	0	0	0	0	0	15	15	15	15	60
		D	3	5	4	2	14	15	15	15	15	60
		E	0	0	0	0	0	15	15	15	15	60
		F	0	0	0	0	0	15	15	15	15	60
		G	0	0	0	0	0	15	15	15	15	60
		Control	-	-	-	-	-	0	2	1	0	3
2 months	Mud	A	0	0	0	0	0	9	15	9	12	45
		C	0	0	0	0	0	11	12	15	13	51
		E	0	0	0	0	0	8	9	15	15	47
		G	0	0	0	0	0	13	10	9	13	45
		Control	-	-	-	-	-	0	2	1	2	5

Mortality results measured against *Anopheles arabiensis,* determined 2 months after the application of the formulation to an area that includes the pest.

Table 7

Mortality Results *Anopheles arabiensis*.

Period after treatment	Test surface	Sample code	Knockdown counts Out of 15					Mortality counts Out of 15				
			Replicates After 30 min.				Total out of 60	Replicates After 24 hours				Total Out of 60
			1	2	3	4		1	2	3	4	
		A	0	0	0	0	0	14	12	13	10	49
		B	0	0	0	0	0	15	15	15	15	60
		C	0	0	0	0	0	15	15	15	15	60

4 months	Gypsum	D	2	0	3	1	6	3	7	4	5	18
		E	0	0	0	0	0	8	10	5	9	32
		F	0	0	0	0	0	10	14	10	13	47
		G	2	1	2	2	7	15	15	15	15	60
		Control	-	-	-	-	-	0	1	1	1	3
	Wood	A	0	0	0	0	0	3	2	5	3	13
		B	0	0	0	0	0	15	15	15	15	60
		C	0	0	0	0	0	15	15	15	15	60
		D	0	0	0	0	0	1	4	2	3	10
		E	0	0	0	0	0	4	11	6	8	29
		F	0	0	0	0	0	2	1	6	3	12
		G	0	0	0	0	0	15	14	14	15	58
		Control	-	-	-	-	-	0	1	0	1	2
4 months	Mud	A	0	0	0	0	0	2	3	3	7	15
		C	0	0	0	0	0	8	6	4	3	21
		E	0	0	0	0	0	2	3	2	1	8
		G	0	0	0	0	0	7	11	5	8	31
		Control	0	0	0	0	0	2	2	0	1	5

Mortality results measured against *Anopheles arabiensis,* determined 4 months after the application of the formulation to an area that includes the pest.

Table 8

Mortality Results *Anopheles arabiensis*.

Period after treatment	Test surface	Sample code	Knockdown counts Out of 15					Mortality counts Out of 15				
			Replicates After 30 min.				Total out of 60	Replicates After 24 hours				Total Out of 60
			1	2	3	4		1	2	3	4	
5 months 3 weeks	Gypsum	A	0	0	0	0	0	9	7	11	10	37
		B	0	0	0	0	0	10	6	9	13	38
		C	0	0	0	0	0	15	15	15	15	60
		F	0	0	0	0	0	3	3	2	1	9
		G	0	0	0	0	0	15	15	15	15	60
		Control	-	-	-	-	-	1	0	2	1	4
	Wood	A	0	0	0	0	0	5	9	8	6	28
		B	0	0	0	0	0	14	15	15	15	59
		C	0	0	0	0	0	15	1	15	15	60
		G	0	0	0	0	0	15	14	15	15	59
		Control	-	-	-	-	-	1	0	1	0	2
5 months 3 weeks	Mud	A	0	0	0	0	0	4	1	2	3	10
		B	0	0	0	0	0	3	7	1	2	13
		C	0	0	0	0	0	5	8	6	4	23
		Control	0	0	0	0	0	0	1	1	3	5

Mortality results measured against *Anopheles arabiensis,* determined 5 months and 3 weeks after the application of the formulation to an area that includes the pest.

Table 9

		Solvent(s)	Amine	Particle Size (VMD, μm)	Wall Thickness (nm)	30 days	60 days	120 days	170 days
Gypsum	A	Solvesso 150	DETA	12	120	60	60	49	37
	B	Solvesso 150	EDA	12	80	60	60	60	38
	C	methyl oleate, Solvesso 150	DETA	12	120	60	60	60	60
	D	methyl oleate, Solvesso 150	EDA	12	80	60	60	18	-
	E	soybean oil, Solvesso 150	DETA	12	120	60	60	32	-
	F	polyglycol P-2000, Solvesso 150	DETA	12	120	60	60	47	-
Wood	A	Solvesso 150	DETA	12	120	60	60	13	28
	B	Solvesso 150	EDA	12	80	60	60	60	59
	C	methyl oleate, Solvesso 150	DETA	12	120	60	60	60	60
	D	methyl oleate, Solvesso 150	EDA	12	80	60	60	10	-
	E	soybean oil, Solvesso 150	DETA	12	120	60	60	29	-
	F	polyglycol P-2000, Solvesso 150	DETA	12	120	60	60	12	-
Mud	A	Solvesso 150	DETA	12	120	44	45	15	10
	B	Solvesso 150	EDA	12	80	34	-	-	13
	C	methyl oleate, Solvesso 150	DETA	12	120	51	21	21	23
	D	methyl oleate, Solvesso 150	EDA	12	80	12	-	-	-
	E	soybean oil, Solvesso 150	DETA	12	120	46	8	8	-
	F	polyglycol P-2000, Solvesso 150	DETA	12	120	11	-	-	-

Summary of residual insecticidal activity measured using mosquitoes. These values were determined after the application of different microcapsule formulations that include an organophosphate insecticide such as chlorpyrifos-methyl. Some of the

formulations included an esterified fatty acid while the other formulations do not include this compound.

[0028] Referring now to Table 9, of all of the formulations tested, the formulations with the longest effective periods of post application activity included esterified fatty acids. The other non-volatile components, such as soybean oil and polyglycol, did not extend the effective field life of the insecticide to the same extent as did the esterified fatty acids. These results demonstrate that the addition of an esterified fatty acid to a microcapsule that includes an organophosphate insecticide creates a microcapsule formulation that retains it insecticidal activity for upwards of 150 days after its application.

Experimental

Materials and Methods

Preparation of Microcapsule Suspensions

[0029] Referring now to Table 1, amounts of the components used to synthesize representative for capsule suspension are summarized in Table 1. The procedure followed to prepare for the compounds listed in Table 1 was as follows. Different formulations were made by changing the composition of the reaction mixture. An organic phase was prepared by combining the indicated amount of PAPI 27 isocyanate monomer (Dow Chemical) with a 50 wt.% solution of chlorpyrifos-methyl in Solvesso 150, also containing 1-nonanal as a preservative. Methyl oleate, soybean oil, or Polyglycol P-2000, were included as indicated in Table 1. This mixture was swirled until homogeneous. An aqueous phase was prepared comprised of the indicated amounts of poly(vinyl alcohol) (PVA, Gohsenol GL03, Nippon Gohsei), Veegum® (R. T. Vanderbilt), and Kelzan S® (Kelco) with the amount of DI water indicated in Table 1 minus the amount utilized to prepare the

10% amine solution described below. This aqueous phase was added to the organic phase to give a two-phase mixture. This mixture was emulsified using a Silverson L4RT-A high-speed mixer using the standard mixing head assembly fitted with the emulsion sleeve. Emulsification was achieved by first mixing at relatively low speed (~1000 rpm) with the tip of the mixing assembly located in the aqueous phase to draw in the organic phase until well emulsified. The speed was then increased in discrete increments. The mixer was stopped after each increase in speed and a size measurement taken. This process was continued until the desired particle size was obtained. A speed of ~4500-7500 rpm was typically required to reach the desired size. The cross-linking amine (either diethylenetriamine (DETA) or ethylenediamine (EDA), Aldrich) was added dropwise as a 10% aqueous solution while stirring at a reduced speed that maintained good mixing. Following the completion of the amine addition, the resulting capsule suspension was stirred for an additional minute, the indicated amount of Atlox 4913 was added, and a final brief homogenization was performed to complete the preparation of the capsule suspension.

[0030] By carefully adjusting the length of time that the mixture is stirred and/or by adjusting the speed of the mixer, it is possible to produce encapsulated organophosphate insecticidal formulations of varying capsule size having a range of shell thicknesses. Similarly, the amounts of monomer, cross-linking agents, wetting agents, buffer, and the like can be adjusted to create microencapsulated organophosphate insecticidal formulations having varying capsule and shell thicknesses.

[0031] The final composition of the microcapsules is equivalent or eventually identified to the proportion of the materials used in their formation. Accordingly, the

composition of these formulations is very similar, if not identical, to the composition of the reaction mixtures used to form them (Table 1).

Measurement of Particle Size in Microcapsule Suspensions

[0032] Capsule suspension particle size distributions were determined using a Malvern Mastersizer 2000 light scattering particle sizer fitted with a small volume sample unit and using software version 5.12. Prior to measurement the samples were shaken or stirred well to insure homogeneity. The volume median distribution (VMD) is reported for each formulation in the Materials section above.

Calculation of Capsule Wall Thickness

[0033] The calculation of the amounts of capsule wall components needed to achieve a target wall thickness was based on the geometric formula relating the volume of a sphere to its radius. If a core-shell morphology is assumed, with the core comprised of the non wall-forming, water insoluble components (chlorpyrifos, solvent) and the shell made up of the polymerizable materials (oil and water soluble monomers), then equation (1) holds, relating the ratio of the volume of the core (V_C) and the volume of the core, plus the volume of the shell (V_S) to their respective radii, where r_S is radius of the capsule including the shell and l_s is thickness of the shell.

$$\frac{V_c + V_s}{V_c} = \left(\frac{r_s}{r_s - l_s} \right)^3 \qquad (1)$$

Solving equation (1) for the volume of the shell yields:

$$V_S = V_C \left(\left(\frac{r_S}{r_S - l_S} \right)^3 - 1 \right) \qquad (2)$$

Substituting masses (m_i) and densities (d_i) for their respective volumes ($m_S / d_S = V_S$ and $m_C / d_C = V_C$, where the subscript s or c refers to the shell or core, respectively) and solving for the mass of the shell gives:

$$m_S = m_C \frac{d_S}{d_C}\left(\left(\frac{r_S}{r_S - l_S}\right)^3 - 1\right) \tag{3}$$

[0034] In order to simplify the calculation and directly use the respective weights of the capsule core and shell components the approximation that the density ratio d_s/d_c is approximately equal to one was made yielding equation (4).

$$m_S \approx m_C\left(\left(\frac{r_S}{r_S - l_S}\right)^3 - 1\right) \tag{4}$$

Making the substitutions $m_C = m_O - m_{OSM}$, $m_S = m_O + (f_{WSM/OSM})m_{OSM} - m_C$, and $f_{WSM/OSM} = m_{WSM} / m_{OSM}$ (the ratio of water soluble monomer to oil soluble monomer), where m_O is the total mass of the oil components (Chloryprifos, solvent, oil-soluble monomer), m_{OSM} is the mass of the oil-soluble monomer, and m_{WSM} is the mass of the water-soluble monomer, and solving for m_{OSM} yields:

$$m_{OSM} = \frac{m_O\left(\left(\frac{r_S}{r_S - l_S}\right)^3 - 1\right)}{f_{WSM/OSM} + \left(\frac{r_S}{r_S - l_S}\right)^3} \tag{5}$$

[0035] For the determination of m_{OSM}, the entire quantity of m_{WSM} was used in the calculation as a convention. In the present study the water-soluble monomer was used on a 1:1 equivalent weight basis relative to the oil-soluble monomer for all of the capsule suspension preparations.

Listing of Various Formulations Synthesized and Tested, see also Table 1.

[0036] A includes 22.4% w/w (240g/i) chlorpyrifos-methyl.

[0037] B includes 22.4% w/w (240g/i) chlorpyrifos-methyl.

[0038] C includes 14.6% w/w (150g/i) chlorpyrifos-methyl.

[0039] D includes 14.6% w/w (150g/i) chlorpyrifos-methyl.

[0040] E includes 14.6% w/w (150g/i) chlorpyrifos-methyl.

[0041] F includes 14.6% w/w (150g/i) chlorpyrifos-methyl.

[0042] DDT-G includes 750 g/kg trichlorobis (chlorophenyl)ethane;

Test Methods

[0043] Insect knockdown tests were carried out using a modified version of the WHO laboratory protocol. In these tests, female 1 day – 5 day old malaria mosquitoes were used as test insects. The test surfaces used were mud from Nduma, Tanzania, wood and gypsum. The mud used in these tests was from the same mud source that is used to construct some huts in Nduma. The mud panels were made by mixing soil and tap water and placing it in plastic molds. The top was flattened and left to dry. Cracks that formed were filled with mud. The gypsum panels were made by mixing gypsum and tap water using the same or substantially the same moulds as were used to create the test mud surfaces. The samples of various formulation were diluted with tap water at the rates given in FIG. 3 Table 3 and were applied with an aerograph spray gun.

[0044] The gypsum and wood panels were sprayed and the first exposure was carried out the following day. The insect exposure tests were repeated using the same surfaces at the following intervals: one month, two months, four months, and

five months 3 weeks (about 170 days). Due to the size of the test and the availability of female 1 day – 5 day old malaria mosquitoes, the test was split into two runs.

[0045] During application of each sample, eight filter papers were also treated. These were placed in a deep freeze at -27ºC for analysis after the following storage periods, i.e., one day, one month, two months, four months, and five months three weeks after treatment. After each exposure, a knockdown count was taken and the mosquitoes were transferred to glass containers. The glass containers were covered with organdie and secured with an elastic band. A piece of cotton wool saturated with a 5% sugar solution was placed on top of the organdie as food. The re-exposures were conducted on those surfaces where a mortality of >70% was obtained in the previous exposure or as deemed necessary during the course of conducting these experiments.

[0046] Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the invention as described herein, including the detailed description which follows, the claims, as well as the appended drawings.

[0047] While the novel technology has been illustrated and described in detail in the figures and foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the preferred embodiments have been shown and described and that all changes and modifications that come within the spirit of the novel technology are desired to be protected. As well, while the novel technology was illustrated using specific examples, theoretical arguments, accounts, and illustrations, these illustrations and the accompanying discussion should by no means be interpreted as limiting the technology. All patents, patent

applications, and references to texts, scientific treatises, publications, and the like referenced in this application are incorporated herein by reference in their entirety.

CLAIMS

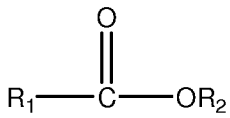
1. A method of extending the effective field life of an insecticide, comprising the steps of:

providing at least one insecticide, at least one esterified fatty acid; at least one cross-linking agent and at least one type of monomer;

mixing the insecticide, the esterified fatty acid, the at least one cross-linking agent and at least one type of monomer; and

forming a polymeric microcapsule shell that at least partially encapsulates a portion of the insecticide and a portion of the esterified fatty acid to form a microencapsulated insecticidal formulation, wherein the microencapsulated insecticidal formulation retains its ability to control insects for at least 1 week after the formulation is applied to an area adjacent to a population of insects.

2. The method according to claim 1, wherein the esterified fatty acid is:



wherein;

R_1 is a straight chain or branched alkyl, or alkenyl group having from 11 to 25 carbon atoms, and R_2 is a straight chain or branched alkyl, or alkenyl group having from 1 to 8 carbon atoms.

3. The method according to claim 1, wherein the esterified fatty acid is methyl oleate.

4. The method according to claim 1, wherein the insecticide is an organophosphate insecticide.

5. The method according to claim 4, wherein the organophosphate insecticide is selected from the group consisting of: acephate, azinphos-methyl, chlorfenvinphos, chlorethoxyfos, chlorpyriphos, diazinon, dimethoate, disulfoton, ethoprophos, fenitrothion, fenthion, fenamiphos, fosthiazate, malathion, methamidophos, methidathion, omethoate, oxydemeton-methyl, parathion, parathion-methyl, phorate, phosmet, profenofos, and trichlorfon.

6. The method according to claim 4, wherein the organophosphate insecticide is chlorpyrifos-methyl.

7. The method according to claim 1, wherein the polymer shell is formed by an interfacial polycondensation and the at least one monomer type includes:

at least one oil soluble monomer selected from the group consisting of: diisocyanates, polyisocyanates, diacid chlorides, poly acid chlorides, sulfonyl chlorides, and chloroformates; and

at least one crosslinking agent selected from the group consisting of: diamines, polyamines, water soluble diols and water soluble polyols.

8. The method according to claim 1, wherein the microcapsule shell has a thickness of between about 90 to about 150 nm.

9. The method according to claim 1, wherein the microcapsule shell has a thickness of about 120 nm.

10. The method according to claim 7, wherein the cross-linking agent is diethylenetriamine.

11. A method for controlling an insect population, comprising the steps of:

providing a microencapsulate insecticide comprising:

at least one esterified fatty acid;

at least one organophosphate insecticide; and

and a polymeric microcapsule shell that at least partially encapsulates the insecticide and the esterified fatty acid; and

applying the microcapsule formulation to an area adjacent to a population of insects, wherein the microencapsulated formulation retains its insecticidal activity for at least 120 days after it is applied to the area adjacent to a population of insects.

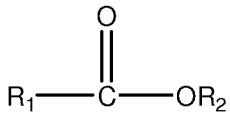
12. The method according to claim 11, wherein the organophosphate insecticide is selected from the group consisting of: acephate, azinphos-methyl, chlorfenvinphos, chlorethoxyfos, chlorpyriphos, diazinon, dimethoate, disulfoton, ethoprophos, fenitrothion, fenthion, fenamiphos, fosthiazate, malathion, methamidophos, methidathion, omethoate, oxydemeton-methyl, parathion, parathion-methyl, phorate, phosmet, profenofos, and trichlorfon.

13. The method according to claim 11, wherein the organophosphate insecticide is chlorpyrifos-methyl.

14. The method according to claim 11, wherein the capsule wall is formed by a interfacial polycondensation between at least one oil soluble monomer selected from the group consisting of: diisocyanates, polyisocyanates, diacid chlorides, poly acid chlorides, sulfonyl chlorides, and chloroformates; and at least one water soluble monomer selected from the group consisting of: diamines, polyamines, water soluble diols and water soluble polyols.

15. The method according to claim 14, wherein the cross-linking agent is diethylenetriamine.

16. The method according to claim 11, wherein the esterified fatty acid is: A



wherein; R_1 is a straight chain or branched alkyl, or alkenyl group having from 11 to 25 carbon atoms, and

R_2 is a straight chain or branched alkyl, or alkenyl group having from 1 to 8 carbon atoms.

17. The method according to claim 16, wherein the esterified fatty acid is methyl oleate.

18. The method according to claim 10, wherein the microcapsule wall has a thickness of between about 90 nm to about 150 nm.

19. The method according to claim 10, wherein the microcapsule has a thickness of about 120 nm.

20. A microencapsulated insecticidal formulation, comprising:

chlorpyrifos-methyl;

methyl oleate; and

and a microcapsule shell, comprising a polyurea.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/025754

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N25/02 A01N25/28 A01N57/16 A01N57/28 A01N57/14
A01N57/12 A01N57/20 A01N57/30 A01N57/32 A01P7/04
ADD.
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)
A01N

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 practical, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	EP 2 090 171 A1 (CHEMINOVA AS [DK]) 19 August 2009 (2009-08-19) page 2, paragraph 0003 - paragraph 0005 page 3, paragraph 0009 - paragraph 0011 page 3, paragraph 0014 - paragraph 0016 paragraph 0019 - page 4, paragraph 0022 page 5, paragraph 0027 examples 1-16	1-20
Y	US 2005/271735 A1 (STOVER HARALD D H [CA] ET AL) 8 December 2005 (2005-12-08) page 1, paragraph 0001 - paragraph 0003 page 1, paragraph 0007 - paragraph 0009 page 3, paragraph 0040 - paragraph 0041 page 10, paragraph 0132 - paragraph 0134 figure 12 figure 13	2,3, 8-16,18, 19

-/--

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
11 May 2010	21/05/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Zanobini, Alessandra

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/025754

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 961 303 A1 (SUMITOMO CHEMICAL CO [JP]) 27 August 2008 (2008-08-27)	1,4-7
Y	claim 1 page 1, paragraph 0005 - paragraph 0008 page 3, paragraph 0019 - paragraph 0025 examples 1-5 text examples 1-3	2,3, 8-16,18, 19
X	FR 2 591 857 A1 (KUREHA CHEMICAL IND CO LTD [JP]) 26 June 1987 (1987-06-26) page 2, line 28 - page 3, line 14 page 5, line 28 - page 6, line 3 example 1 tables 3-5	1,4,5
A	EP 0 368 576 A2 (KUREHA CHEMICAL IND CO LTD [JP]) 16 May 1990 (1990-05-16) the whole document	1-20
A	WO 2009/001076 A1 (SYNGENTA PARTICIPATION AG [CH]; SYNGENTA LTD [GB]; BYWATER ANDREW [CH]) 31 December 2008 (2008-12-31) the whole document	1-20
A	WO 2009/000545 A2 (ENDURA SPA [IT]; SIPCAM S P A [IT]; GOBBI CARLOTTA [IT]; BASSETTI LUCI) 31 December 2008 (2008-12-31) page 12 example 15 example 16A	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2010/025754

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2090171 A1	19-08-2009	WO 2009097860 A1	13-08-2009
US 2005271735 A1	08-12-2005	NONE	
EP 1961303 A1	27-08-2008	AU 2006324753 A1	21-06-2007
		CN 101330826 A	24-12-2008
		WO 2007069461 A1	21-06-2007
		KR 20080077683 A	25-08-2008
		US 2009142406 A1	04-06-2009
FR 2591857 A1	26-06-1987	IT 1228244 B	05-06-1991
		JP 1806119 C	26-11-1993
		JP 5017882 B	10-03-1993
		JP 62149607 A	03-07-1987
		PH 23583 A	11-09-1989
EP 0368576 A2	16-05-1990	AU 605698 B2	17-01-1991
		AU 4433489 A	21-06-1990
		DE 68925562 D1	14-03-1996
		DE 68925562 T2	19-09-1996
WO 2009001076 A1	31-12-2008	AR 067166 A1	30-09-2009
		EP 2170047 A1	07-04-2010
		PE 04642009 A1	24-05-2009
		UY 31181 A1	30-04-2009
WO 2009000545 A2	31-12-2008	AU 2008267383 A1	31-12-2008
		CN 101677532 A	24-03-2010
		EP 2161991 A2	17-03-2010