

(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. **AU 2006330918 B2**

(54) Title
Insecticidal and miticidal mixtures of bifenthrin and cyano-pyrethroids

(51) International Patent Classification(s)
A01N 53/00 (2006.01)

(21) Application No: **2006330918** (22) Date of Filing: **2006.12.21**

(87) WIPO No: **WO07/076028**

(30) Priority Data

(31) Number	(32) Date	(33) Country
60/752,979	2005.12.22	US

(43) Publication Date: **2007.07.05**

(44) Accepted Journal Date: **2012.01.12**

(71) Applicant(s)
FMC Corporation

(72) Inventor(s)
Garcia, Hylsa;Walmsley, Mark;Heim, D. Craig;Hilton, Nancy;Yang, Hui S.;Staetz, Charles A.;Herrick, Robert M.

(74) Agent / Attorney
Watermark Patent and Trade Marks Attorneys, Level 2 302 Burwood Road, Hawthorn, VIC, 3122

(56) Related Art
WO 2003/053345
US 4997970
US 2005/0049146

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

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 July 2007 (05.07.2007)

PCT

(10) International Publication Number
WO 2007/076028 A2

- (51) **International Patent Classification:**
A01N 35/04 (2006.01)
- (54) **Agents:** SHEEHAN, John, M. et al.; FMC CORPORATION, 1735 Market Street, Philadelphia, PA 19103 (US).
- (21) **International Application Number:**
PCT/US2006/049062
- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, 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, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (22) **International Filing Date:**
21 December 2006 (21.12.2006)
- (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, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
60/752,979 22 December 2005 (22.12.2005) US
- (71) **Applicant** (for all designated States except US): **FMC CORPORATION** [US/US]; 1735 Market Street, Philadelphia, PA 19103 (US).
- Published:**
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*
- (72) **Inventors; and**
- (75) **Inventors/Applicants** (for US only): **HERRICK, Robert, M.** [US/US]; 11 Wolfpack Court, Hamilton, NJ 08619-1156 (US). **WALMSLEY, Mark** [US/US]; 1 Dorothy Drive, Morristown, NJ 07960 (US). **STAETZ, Charles, A.** [US/US]; 85 Hickory Lane, Newtown, PA 18940 (US). **HILTON, Nancy** [US/US]; 2020 Walnut Street, Apt. 21G, Philadelphia, PA 19103 (US). **YANG, Hui, S.** [CN/US]; 6 Daisy Court, Plainsboro, NJ 08536 (US). **HEIM, D., Craig** [US/US]; 16 Locust Avenue, Westmont, NJ 08108 (US). **GARCIA, Hylsa** [US/US]; 918 McLain Street, Elizabeth, NJ 07202 (US).



WO 2007/076028 A2

(54) **Title:** INSECTICIDAL AND MITICIDAL MIXTURES OF BIFENTHRIN AND CYANO-PYRETHROIDS

(57) **Abstract:** The present invention is directed to novel insecticidal and/or miticidal compositions comprising bifenthrin and a cyano-pyrethroid. The compositions exhibit an unexpected increase in insecticidal activity as compared to the insecticidal activity of the individual components.

**INSECTICIDAL AND MITICIDAL COMPOSITIONS OF BIFENTHRIN
AND CYANO-PYRETHROIDS**

5 This application claims the benefit of U.S. Provisional Application No. 60/752,979 filed December 22, 2005.

FIELD OF THE INVENTION

10 The present invention relates to the field of insecticides. In particular, the invention provides novel insecticidal compositions comprising bifenthrin and a cyano-pyrethroid that exhibit unexpected insecticidal activity.

BACKGROUND OF THE INVENTION

15 It is well known that insects in general can cause significant damage, not only to crops grown in agriculture, but also, for example, to structures and turf where the damage is caused by soil-borne insects, such as termites and white grubs. Such damage may result in the loss of millions of dollars of value associated with a given crop, turf or structure. Insecticides and acaricides are useful for controlling
20 insects and acarids which may otherwise cause significant damage to crops such as wheat, corn, soybeans, potatoes, and cotton to name a few. For crop protection, it is desirable to use effective chemical insecticides and acaricides which can control the insects and acarids without damaging the crops, and which have no deleterious effects to mammals and other living organisms.

25 For commercial agricultural use it would be of benefit to combine insecticides that have somewhat different spectrums of activity and residual effectiveness in order to benefit from each of the individual insecticidal properties. Mixtures containing two or more insecticides have been practiced in the art in order to benefit from the insecticidal properties of the individual components. For
30 example, U. S. Patent 3,899,586 discloses an insecticidal and/or acaricidal composition obtained by mixing N-(3,4,5,6-tetrahydrophthalimide)-methyl chrysanthemate with 5-(2-propynyl)furfuryl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate.

35

SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that a novel insecticidal composition comprising bifenthrin and a cyano-pyrethroid exhibits an unexpected increase in insecticidal activity as compared to the insecticidal activity of the individual components. The present invention is also directed to a novel insecticidal composition comprising bifenthrin and a cyano-pyrethroid in admixture with at least one agriculturally acceptable extender or adjuvant.

An aspect of the present invention provides a miticidal composition including bifenthrin and a cyano-pyrethroid selected from the group consisting of deltamethrin, cyfluthrin, *alpha*-cypermethrin, *zeta*-cypermethrin, *lambda*-cyhalothrin, and esfenvalerate, wherein the weight ratio of bifenthrin to cyano-pyrethroid is from 10:1 to 1:30.

A further aspect of the present invention provides a method for controlling unwanted insects or mites including applying above mentioned miticidal composition to the foliar portion of a plant.

A further aspect of the present invention provides a foliar insecticidal or miticidal composition including bifenthrin and a cyano-pyrethroid selected from the group consisting of deltamethrin, cyfluthrin, *apha*-cypermethrin, *zeta*-cypermethrin, *lambda*-cyhalothrin, and esfenvalerate, wherein the weight ratio of bifenthrin to cyano-pyrethroid is from 10:1 to 1 :30.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, it has now been found that a novel insecticidal composition comprising bifenthrin and a cyano-pyrethroid exhibit an unexpected increase in insecticidal activity as compared to the insecticidal activity of the individual components. The present invention is also directed to a novel insecticidal composition comprising bifenthrin and a cyano-pyrethroid in admixture with at least one agriculturally acceptable extender or adjuvant.

Synthetic pyrethroids which contain a cyano group (cyano-pyrethroids) are very potent insecticides, for example, *zeta*-cypermethrin is a potent and quick acting insecticide, which controls a broad spectrum of chewing, sucking and flying insects. In addition to controlling chewing, sucking and flying insects, the

pyrethroid bifenthrin is also active against a number of key mite pests and exhibits a longer residual activity than *zeta*-cypermethrin. It has now been discovered that by combining these two potent insecticides, an unexpected increase in insecticidal activity is observed in certain insect species. In addition to being very potent and quick acting insecticides, cyano-pyrethroids often cause mammalian skin irritation. By using a mixture which contains less bifenthrin and less cyano-pyrethroid to achieve insecticidal activity superior to either insecticidal compound alone, an ecological and mammalian safety benefit is realized.

Specifically, one aspect of the present invention is directed to an insecticidal composition comprising bifenthrin and a cyano-pyrethroid.

Another aspect of the present invention is directed to an insecticidal composition comprising bifenthrin and a cyano-pyrethroid, in admixture with at least one agriculturally acceptable extender or adjuvant.

Another aspect of the present invention relates to methods of controlling insects by applying an insecticidally effective amount of a composition as set forth above to a locus of crops such as, without limitation, cereals, cotton, vegetables, and fruits, or other areas where insects are present or are expected to be present.

5 The term "bifenthrin" means 2-methylbiphenyl-3-ylmethyl (Z)-(1RS)-*cis*-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethyl cyclopropanecarboxylate.

The term "cyano-pyrethroid" means an insecticidal pyrethroid that contains a cyano group. The cyano-pyrethroid is selected from the group consisting of, but not limited to:

10 acrinathrin which is (S)- α -cyano-3-phenoxybenzyl (Z)-(1R)-*cis*-2,2-dimethyl-3-[2-(2,2,2-trifluoro-1-trifluoromethylethoxycarbonyl)vinyl]cyclopropanecarboxylate,

 cycloprothrin which is (RS)- α -cyano-3-phenoxybenzyl (RS)-2,2-dichloro-1-(4-ethoxyphenyl)cyclopropanecarboxylate], deltamethrin [(S)- α -cyano-3-
15 phenoxybenzyl (1R)-*cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate,

 tralomethrin which is (S)- α -cyano-3-phenoxybenzyl (1R)-*cis*-2,2-dimethyl-3-[(RS)-1,2,2,2-tetrabromoethyl]cyclopropanecarboxylate,

20 fenvalerate which is (RS)- α -cyano-3-phenoxybenzyl (RS)-2-(4-chlorophenyl)-3-methylbutyrate,

 cyfluthrin which is (RS)- α -cyano-4-fluoro-3-phenoxybenzyl (1RS)-*cis-trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate,

 beta-cyfluthrin which is a reaction mixture comprising the enantiomeric pair (R)- α -cyano-4-fluoro-3-phenoxybenzyl (1S)-*cis*-3-(2,2-dichlorovinyl)-2,2-
25 dimethylcyclopropanecarboxylate and (S)- α -cyano-4-fluoro-3-phenoxybenzyl (1R)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate in ratio 1:2 with the enantiomeric pair (R)- α -cyano-4-fluoro-3-phenoxybenzyl (1S)-*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (S)- α -cyano-4-fluoro-3-phenoxybenzyl (1R)-*trans*-3-(2,2-dichlorovinyl)-2,2-
30 dimethylcyclopropanecarboxylate,

flucythrinate which is (RS)- α -cyano-3-phenoxybenzyl (S)-2-(4-difluoromethoxyphenyl)-3-methylbutyrate,

alpha-cypermethrin which is a racemate comprising (S)- α -cyano-3-phenoxybenzyl (1R)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
5 and (R)- α -cyano-3-phenoxybenzyl (1S)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate,

beta-cypermethrin which is a reaction mixture comprising two enantiomeric pairs in a ratio of about 2:3 (S)- α -cyano-3-phenoxybenzyl (1R)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (R)- α -cyano-3-phenoxybenzyl (1S)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
10 with (S)- α -cyano-3-phenoxybenzyl (1R)-*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (R)- α -cyano-3-phenoxybenzyl (1S)-*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate,

theta-cypermethrin which is a 1:1 mixture of the enantiomers (R)- α -cyano-3-phenoxybenzyl (1S)-*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate and (S)- α -cyano-3-phenoxybenzyl (1R)-*trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate,
15

zeta-cypermethrin which is (R,S)- α -cyano-3-phenoxybenzyl-(1RS)-*cis-trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate which has been
20 enriched in the 1R-*cis*-S and 1R-*trans*-S isomers,

cyphenothrin which is (R,S)- α -cyano-3-phenoxybenzyl-(1R)-*cis-trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate,

cyhalothrin which is (R,S)- α -cyano-3-phenoxybenzyl-(Z)-(1RS)-*cis*-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate,

lambda- cyhalothrin which is a reaction product comprising equal quantities of (S)- α -cyano-3-phenoxybenzyl-(Z)-(1R)-*cis*-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate and (R)- α -cyano-3-phenoxybenzyl-(Z)-(1S)-*cis*-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate,
25

esfenvalerate which is (S)- α -cyano-3-phenoxybenzyl (S)-2-(4-chlorophenyl)-3-methylbutyrate,
30

fluvalinate which is (*RS*)- α -cyano-3-phenoxybenzyl *N*-(2-chloro- α,α,α -trifluoro-*p*-tolyl)-DL-valinate, and

fenpropathrin which is (*RS*)- α -cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate.

5 A particular form of *zeta*-cypermethrin is (*R,S*)- α -cyano-3-phenoxybenzyl-(1*RS*)-*cis-trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate which has been enriched in the 1*R-cis-S* and 1*R-trans-S* isomers by the processes disclosed in patents U. S. 5,164,411, U. S. 5,028,731 and U. S. 4,997,970. A most preferred form of *zeta*-cypermethrin is the isomer mixture prepared by the process disclosed in
10 U. S. 4,997,970 starting with a 55/45 *cis/trans* mixture of cypermethrin with a catalytic amount of tricapyrylammonium chloride (Aliquat[®] 336, Aldrich Chemical Co.) and sodium carbonate in *n*-heptane. This process and subsequent isolation procedure produces *zeta*-cypermethrin containing a small amount, usually 0.6% to 1.3%, of the catalyst.

15 The ratio of bifenthrin active ingredient (AI) to cyano-pyrethroid AI may be from 1/99 to 99/1. Preferably the ratio of bifenthrin AI to cyano-pyrethroid AI is from 1/4 to 4/1. More preferably the ratio is from 1/3 to 3/1.

The present composition is effective against various insect pests and/or acarina pests. Insect pests and acarina pests to which the present composition can be
20 applied are: Homoptera, which includes, for example, aphids, leafhoppers, cicadas, whiteflies, and mealybugs; Lepidoptera, which includes, for example, butterflies, moths and skippers; Coleoptera, which includes, for example, beetles and weevils; and Acarina, which includes, for example, mites and ticks.

These insecticidal compositions may be applied either as water-diluted
25 sprays, or dusts, or granules to the areas in which suppression of insects is desired. These formulations may contain as little as 0.1%, 0.2% or 0.5% to as much as 95% or more by weight of active ingredient.

Dusts are free flowing admixtures of the active ingredient with finely divided solids such as talc, natural clays, kieselguhr, flours such as walnut shell and
30 cottonseed flours, and other organic and inorganic solids which act as dispersants and carriers for the toxicant; these finely divided solids have an average particle size

of less than about 50 microns. A typical dust formulation useful herein is one containing 1.0 part or less of the insecticidal compound and 99.0 parts of talc.

Wettable powders, also useful formulations for insecticides, are in the form of finely divided particles that disperse readily in water or other dispersant. The wettable powder is ultimately applied to the locus where insect control is needed either as a dry dust or as an emulsion in water or other liquid. Typical carriers for wettable powders include Fuller's earth, kaolin clays, silicas, and other highly absorbent, readily wet inorganic diluents. Wettable powders normally are prepared to contain about 5-80% of active ingredient, depending on the absorbency of the carrier, and usually also contain a small amount of a wetting, dispersing or emulsifying agent to facilitate dispersion. For example, a useful wettable powder formulation contains 80.0 parts of the insecticidal compound, 17.9 parts of Palmetto clay, and 1.0 part of sodium lignosulfonate and 0.3 part of sulfonated aliphatic polyester as wetting agents. Additional wetting agent and/or oil will frequently be added to a tank mix for to facilitate dispersion on the foliage of the plant.

Other useful formulations for insecticidal applications are emulsifiable concentrates (ECs) which are homogeneous liquid compositions dispersible in water or other dispersant, and may consist entirely of the insecticidal compound and a liquid or solid emulsifying agent, or may also contain a liquid carrier, such as xylene, heavy aromatic naphthas, isophorone, or other non-volatile organic solvents. For insecticidal application these concentrates are dispersed in water or other liquid carrier and normally applied as a spray to the area to be treated. The percentage by weight of the essential active ingredient may vary according to the manner in which the composition is to be applied, but in general comprises 0.5 to 95% of active ingredient by weight of the insecticidal composition.

Flowable formulations and concentrated aqueous emulsion formulations (EWs) are similar to ECs, except that the active ingredient is suspended in a liquid carrier, generally water. Flowables, like ECs, may include one or more surfactants, and will typically contain active ingredients in the range of 0.5 to 95%, frequently from 10 to 50%, by weight of the composition. For application, flowables may be diluted in water or other liquid vehicle, and are normally applied as a spray to the area to be treated.

Typical wetting, dispersing or emulsifying agents used in agricultural formulations include, but are not limited to, the alkyl and alkylaryl sulfonates and sulfates and their sodium salts; alkylaryl polyether alcohols; sulfated higher alcohols; polyethylene oxides; sulfonated animal and vegetable oils; sulfonated
5 petroleum oils; fatty acid esters of polyhydric alcohols and the ethylene oxide addition products of such esters; and the addition product of long-chain mercaptans and ethylene oxide. Many other types of useful surface-active agents are available in commerce. Surface-active agents, when used, normally comprise 1 to 15% by weight of the composition.

10 Other useful formulations include suspensions of the active ingredient in a relatively non-volatile solvent such as water, corn oil, kerosene, propylene glycol, or other suitable solvents.

Still other useful formulations for insecticidal applications include simple solutions of the active ingredient in a solvent in which it is completely soluble at the
15 desired concentration, such as acetone, alkylated naphthalenes, xylene, or other organic solvents. Granular formulations, wherein the toxicant is carried on relative coarse particles, are of particular utility for aerial distribution or for penetration of cover crop canopy. Pressurized sprays, typically aerosols wherein the active ingredient is dispersed in finely divided form as a result of vaporization of a low-
20 boiling dispersant solvent carrier may also be used. Water-soluble or water-dispersible granules are free flowing, non-dusty, and readily water-soluble or water-miscible. In use by the farmer on the field, the granular formulations, emulsifiable concentrates, flowable concentrates, aqueous emulsions, solutions, etc., may be diluted with water to give a concentration of active ingredient in the range of say
25 0.1% or 0.2% to 1.5% or 2%.

Insecticide formulations may further comprise additional components such as an anti-freeze agent, an anti-foam agent and /or a biocide.

The compositions of the present invention are further illustrated by the examples below. The examples serve only to illustrate the invention and should not
30 be interpreted as limiting since further modifications of the disclosed invention will be apparent to those skilled in the art. All such modifications are deemed to be within the scope of the invention as defined in the claims.

The term "ambient temperature" as utilized herein means any suitable temperature found in a laboratory or other working quarter, and is generally not below about 15° C nor above about 30° C.

5

Example 1

This example illustrates one protocol for the preparation of a 2/1 ratio of bifenthrin to *zeta*-cypermethrin emulsifiable concentrate formulation

To 42.32 grams of Aromatic 200 ND (available from ExxonMobile Chemicals) was added 8.34 grams of melted bifenthrin (95.9% active ingredient) and 11.11 grams of *zeta*-cypermethrin (36% active ingredient, prepared by the process disclosed in U. S. Patent 4,997,970). The mixture was stirred at ambient temperature with a mechanical stirrer until a homogenous solution formed, at which time 2.52 grams of a branched dodecylbenzene sulfonate salt (Agnique ABS 70AE, available from Cognis Corporation), 0.28 gram of polyethylene glycol monooleate (Agnique PEG 400MO, available from Cognis Corporation) 0.84 gram of ethoxylated castor oil (Agnique CSO-36, available from Cognis Corporation), 1.96 grams ethoxylated castor oil (Agnique CSO-25, available from Cognis Corporation), 20.00 grams of severely solvent refined light and heavy paraffinic petroleum oil (Sunspray 6N, available from Sunoco, Inc.) and 0.08 gram of acetic acid were added. Upon completion of the addition, the agitation was continued for 10 minutes to obtain a yellowish homogeneous solution.

Candidate insecticide compositions were evaluated for activity in foliar evaluations against tobacco budworm (*Heliothis virescens* [Fabricius]), Colorado potato beetle (*Leptinotarsa decemlineata* [Say]), corn earworm (*Helicoverpa zea* [Boddie]), cotton aphid (*Aphis gossypii* [Glover]) and twospotted spider mite (*Tetranychus urticae* [Koch]). Each test included controls in which the formulation or test solution minus the active ingredients were applied.

In tests against tobacco budworm, the first true leaves of 7 to 10 day-old cotton plants (*Gossypium hirsutum*) were dipped into the test solutions of the test formulations to provide application rates as high as 10 ppm of the active ingredients, bifenthrin and *zeta*-cypermethrin (prepared by the process disclosed in U. S. Patent 4,997,970). The test formulations were dissolved in distilled water containing 10% acetone and 0.25% of a non-ionic detergent [an

octylphenolpoly(ethyleneglycolether)_x, available from Roche Applied Science as Triton X-100] to the proper concentrations. The treated plants were transferred to a hood where they were kept until the leaves had dried.

Each leaf was placed into a separate (100 x 20 mm) plastic Petri dish, containing a water-moistened filter paper. Five second-instar (7 day-old) tobacco budworms were placed into each Petri dish, taking care not to cause injury. The plastic lids were placed on each of the dishes, which were then held for 72 hours at 25°C, 50% relative humidity with a photo-period of 12 hours light and 12 hours dark. At the end of the 72 hour exposure period, the dishes were opened, and the numbers of dead and live insects were counted. Insects were classified as "dead" if they failed to rapidly right themselves when turned over. Using the insect counts, the activity of the test chemical was expressed in percent control. Percent control is derived from the total number of dead insects (TD) compared to the total number of insects (TI) in the test:

$$\% \text{ Control} = \frac{TD}{TI} \times 100.$$

In tests against adult Colorado potato beetle, the leaves of 6 – 8 inch tall tomato plants (*Lycopersicon lycoper*) were dipped into the test solutions of the test formulations to provide application rates as high as 1000 ppm of the active ingredients. The test formulations were dissolved in distilled water containing 10% acetone and 0.25% of a non-ionic detergent [an octylphenolpoly(ethyleneglycolether)_x, available from Roche Applied Science as Triton X-100] to the proper concentrations. The treated plants were transferred to a hood where they were kept until the leaves had dried. For tests in which the active ingredients were not formulated, i.e. the technical active ingredient was used; a stock solution of the test compound was made. For example, a 100ppm stock solution may be made by dissolving 4 milligrams of the test compound in 4 mL of acetone and adding the solution to 36 mL of an aqueous Triton X-100 solution (one drop of Triton X-100 dissolved in 100 mL of distilled water). Further dilutions can be made by adding distilled water containing 10% acetone and 0.25% of Triton X-100.

The treated tomato plants were removed from their pots by cutting the stems just above the soil line. Each excised plant was placed into an individual 8-ounce

paper cup. Ten adult Colorado potato beetles were placed into each paper cup, taking care not to cause injury. An opaque plastic lid was placed on each cup, for a 72 hour exposure period and held at 25°C, 50% relative humidity with a photoperiod of 12 hours light and 12 hours dark. At the end of the 72 hour exposure period, the cups were opened, and the numbers of dead and live insects were counted. Using the insect counts, the activity of the test chemical was expressed in percent control. Percent control is derived from the total number of dead insects (TD) compared to the total number of insects (TI) in the test:

$$\% \text{ Control} = \frac{TD}{TI} \times 100.$$

10

In tests against corn earworm, one inch diameter leaf discs cut from cotton plant leaves (*Gossypium hirsutum*) were dipped into the test solutions of the test formulations to provide application rates as high as 1000 ppm of the active ingredients. The test formulations were dissolved in distilled water containing 10% acetone and 0.25% of a non-ionic detergent [an octylphenolpoly(ethyleneglycolether)_x, available from Roche Applied Science as Triton X-100] to the proper concentrations. Cotton wicks, 0.5 inch diameter by 2 inches long, were soaked with distilled water and placed into the wells of a 32 well rearing tray (available as Rearing Tray Bio-Fit 32, from C-D International, Pittman, New Jersey), one wick per well. Treated leaf discs were placed on top of the cotton wicks, one leaf disc per wick, and the rearing tray was transferred to a hood where they were kept until the leaf discs had dried. Each disc was infested with 1 late second to early third instar corn earworm, replicated sixteen times per rate of application, and a lid was placed on the rearing tray. The rearing trays were held in a growth chamber for 96 hours at 25°C, 50% relative humidity and a photoperiod of 12 hours light/12 hours dark. For tests in which the active ingredients were not formulated, i.e. the technical active ingredient was used; a stock solution of the test compound was made. For example, a 100ppm stock solution may be made by dissolving 4 milligrams of the test compound in 4 mL of acetone and adding the solution to 36 mL of an aqueous Triton X-100 solution (one drop of Triton X-100 dissolved in 100 mL of

20
25
30

distilled water). Further dilutions can be made by adding distilled water containing 10% acetone and 0.25% of Triton X-100.

At the end of the 96 hour exposure period, the rearing tray was opened, and the numbers of dead and live insects were counted. Insects were classified as "dead" if they failed to show movement when probed. Using the insect counts, the activity of the test chemical was expressed in percent control. Percent control is derived from the total number of dead insects (TD) compared to the total number of insects (TI) in the test:

$$\% \text{ Control} = \frac{TD}{TI} \times 100.$$

In tests against cotton aphid, the leaves of 6 to 8 inch tall tomato plants (*Lycopersicon lycoper*) were infested with about 50 cotton aphids by placing leaf cuttings from a cotton aphid colony host tomato plant. After about 12 hours the newly infested tomato leaves were dipped into the test solutions of the test formulations to provide application rates as high as 1000 ppm of the active ingredients. The test formulations were dissolved in, and diluted as necessary, with distilled water containing 10% acetone and 0.25% of a non-ionic detergent [an octylphenolpoly(ethyleneglycolether)_x, available from Roche Applied Science as Triton X-100] to the proper concentrations. After treatment, a square of parafilm was placed around the stem of each test plant, covering the soil of each pot in order to catch dead aphids that fall from the leaves. The treated plants were transferred to a hood where they were kept until the leaves had dried. Once dry, the potted plants were placed into a tray containing at least one inch of water. The plants were spaced far enough apart to prevent the aphids from moving between plants. The trays were held in a growth chamber for 72 hours at 25°C, 50% relative humidity and a photoperiod of 14 hours light/10 hours dark. For tests in which the active ingredients were not formulated, i.e. the technical active ingredient was used; a stock solution of the test compound was made. For example, a 100ppm stock solution may be made by dissolving 4 milligrams of the test compound in 4 mL of acetone and adding the solution to 36 mL of an aqueous Triton X-100 solution (one drop of Triton X-100 dissolved in 100 mL of distilled water). Further dilutions can be made by adding distilled water containing 10% acetone and 0.25% of Triton X-100.

At the end of the 72 hour exposure period the numbers of dead and live insects were counted. Insects were classified as "dead" if they were off-color or brown and desiccated. Using the insect counts, the activity of the test chemical was expressed in percent control. Percent control is derived from the total number of dead insects (TD) compared to the total number of insects (TI) in the test:

$$\% \text{ Control} = \frac{TD}{TI} \times 100.$$

In tests against twospotted spider mites, the leaves of potted 3 to 4 inch tall pinto bean plants (*Phaseolus vulgaris*) were infested with about 50 to 75 adult twospotted spider mites by placing leaf cuttings from a twospotted spider mite colony host pinto bean plant on the upper surface of the test plant leaves. After about 1 hour the newly infested pinto bean leaves were dipped into the test solutions of the test formulations to provide application rates as high as 1000 ppm of the active ingredients. The test formulations were dissolved in, and diluted as necessary, with distilled water containing 10% acetone and 0.25% of a non-ionic detergent [an octylphenolpoly(ethyleneglycolether)_x, available from Roche Applied Science as Triton X-100] to the proper concentrations. The treated plants were transferred to a hood where they were kept until the leaves had dried. Once dry, the potted plants were placed into a tray containing at least one inch of water. The plants were spaced far enough apart to prevent the mites from moving between plants. The trays were held in a growth chamber for 96 hours at 25°C, 50% relative humidity and a photoperiod of 14 hours light/10 hours dark. For tests in which the active ingredients were not formulated, i.e. the technical active ingredient was used; a stock solution of the test compound was made. For example, a 100ppm stock solution may be made by dissolving 4 milligrams of the test compound in 4 mL of acetone and adding the solution to 36 mL of an aqueous Triton X-100 solution (one drop of Triton X-100 dissolved in 100 mL of distilled water). Further dilutions can be made by adding distilled water containing 10% acetone and 0.25% of Triton X-100.

At the end of the 96 hour exposure period the numbers of dead and live insects were counted. Insects were classified as "dead" if they failed to show movement when probed. Using the insect counts, the activity of the test chemical

was expressed in percent control. Percent control is derived from the total number of dead insects (TD) compared to the total number of insects (TI) in the test:

$$\% \text{ Control} = \frac{TD}{TI} \times 100.$$

Tobacco budworm insecticidal activity data at selected rates of application
5 from this test are provided in Table 2. Adult Colorado potato beetle insecticidal
activity data at selected rates of application from this test are provided in Table 3.
Tables 2 and 3 also contain insecticidal results from individually tested formulations
of bifenthrin (Capture 2EC[®], available from FMC Corporation), and *zeta*-
cypermethrin (Mustang Max 0.8EC[®], available from FMC Corporation) as well as
10 the control test results. For all cases reported in Tables 2 and 3, the test insecticide
formulation comprised, % by weight of all components in the total formulation and
(grams): 15.00% (19.45 grams) bifenthrin/*zeta*-cypermethrin (ratio of
bifenthrin/*zeta*-cypermethrin provided in the table), 7.00% (5.60 grams) of the
surfactant blend, 25.00% (20.00 grams) of Sunspray 6N, 52.90% (42.32 grams) of
15 aromatic 200, and 0.10% (0.08 gram) of acetic acid. The surfactant blend comprised
3.15% (2.52 grams) of Agnique ABS70AE, 0.35% (0.28 gram) of Agnique PEG 400
MO, 1.05% (0.84 gram) of Agnique CSO-36, and 2.45% (1.96 grams) of Agnique
CSO-25. The bold numbers indicate that a beneficial insecticidal effect was
observed when compared to the individual compounds.

20

Table 2

Tobacco Budworm (*Heliothis virescens* [Fabricius]) Insecticidal Activity of
Bifenthrin and *zeta*-Cypermethrin (prepared by the process disclosed in U. S. Patent
4,997,970)

Treatment	Bifenthrin/ <i>zeta</i> - Cypermethrin Ratio	Concentration Bifenthrin (ppm)	Concentration <i>zeta</i> - Cypermethrin (ppm)	Total Concentration (ppm)	Percent Mortality
Capture 2EC [®]	1/0	10.0	0	10.0	100
Capture 2EC [®]	1/0	5.4	0	5.4	95
Capture 2EC [®]	1/0	3.0	0	3.0	35
Capture 2EC [®]	1/0	1.0	0	1.0	20
Mustang Max 0.8EC [®]	0/1	0	10.0	10.0	90
Mustang Max 0.8EC [®]	0/1	0	5.4	5.4	65
Mustang Max 0.8EC [®]	0/1	0	3.0	3.0	40
Mustang Max 0.8EC [®]	0/1	0	1.0	1.0	30
Bifen/ <i>zeta</i>	2/1	6.7	3.3	10.0	95
Bifen/ <i>zeta</i>	2/1	3.6	1.8	5.4	90
Bifen/ <i>zeta</i>	2/1	2.0	1.0	3.0	80
Bifen/ <i>zeta</i>	2/1	0.7	0.3	1.0	55
Bifen/ <i>zeta</i>	1/1	5.0	5.0	10.0	90
Bifen/ <i>zeta</i>	1/1	2.7	2.7	5.4	85
Bifen/ <i>zeta</i>	1/1	1.5	1.5	3.0	70
Bifen/ <i>zeta</i>	1/1	.05	.05	1.0	40
Bifen/ <i>zeta</i>	1/2	3.3	6.7	10.0	100
Bifen/ <i>zeta</i>	1/2	1.8	3.6	5.4	90
Bifen/ <i>zeta</i>	1/2	1.0	2.0	3.0	75
Bifen/ <i>zeta</i>	1/2	0.3	0.7	1.0	35
Bifen/ <i>zeta</i>	1/3	2.5	7.5	10.0	90
Bifen/ <i>zeta</i>	1/3	1.4	4.1	5.4	79
Bifen/ <i>zeta</i>	1/3	0.8	2.3	3.0	85
Bifen/ <i>zeta</i>	1/3	0.3	0.8	1.0	65
Bifen/ <i>zeta</i>	1/4	2.0	8.0	10.0	100
Bifen/ <i>zeta</i>	1/4	1.1	4.3	5.4	95
Bifen/ <i>zeta</i>	1/4	0.6	2.4	3.0	85
Bifen/ <i>zeta</i>	1/4	0.2	0.8	1.0	56
Control	-	0	0	0	0

As set forth in Table 2, test formulations of bifenthrin and *zeta*-cypermethrin at
5 total concentrations of 3.0 ppm and lower provided better control of the tobacco
budworm when compared to the individually tested formulations of bifenthrin
(Capture 2EC[®], available from FMC Corporation), and *zeta*-cypermethrin (Mustang
Max 0.8EC[®], available from FMC Corporation). One skilled in the art would expect

the mixtures of bifenthrin and *zeta*-cypermethrin, at lower than normal use rates, to exhibit equivalent insecticidal activity to that of the individual insecticidal compounds. At rates of 3.0 ppm and lower, the novel formulated mixture exhibited up to twice the insecticidal activity of the insecticidal compounds at those rates and is within the insecticidal activity of the commercially suggested rates of 5.4 ppm and 10.0 ppm.

Table 3

Adult Colorado potato beetle (*Leptinotarsa decemlineata* [Say]) Insecticidal Activity of Bifenthrin and *zeta*-Cypermethrin (prepared by the process disclosed in U. S. Patent 4,997,970)

Treatment	Bifenthrin/ <i>zeta</i> - Cypermethrin Ratio	Concentration Bifenthrin (ppm)	Concentration <i>zeta</i> - Cypermethrin (ppm)	Total Concentration (ppm)	Percent Mortality
Capture 2EC®	1/0	10.0	0	10.0	35
Mustang Max 0.8EC®	0/1	0	10.0	10.0	30
<i>Bifen/zeta</i>	2/1	6.7	3.3	10.0	90
<i>Bifen/zeta</i>	1/1	5.0	5.0	10.0	95
<i>Bifen/zeta</i>	1/2	3.3	6.7	10.0	70
<i>Bifen/zeta</i>	1/3	2.5	7.5	10.0	70
<i>Bifen/zeta</i>	1/4	2.0	8.0	10.0	65
Control	-	0	0	0	0

As set forth in Table 3, test formulations of bifenthrin and *zeta*-cypermethrin, at a total concentration of 10.0 ppm, provided better control of the Colorado potato beetle when compared to the individually tested formulations of bifenthrin (Capture 2EC®, available from FMC Corporation) and *zeta*-cypermethrin (Mustang Max 0.8EC®, available from FMC Corporation). One skilled in the art would expect the mixtures of bifenthrin and *zeta*-cypermethrin to exhibit insecticidal activity equivalent to that of the individual insecticidal compounds. At the tested rate of 10.0 ppm, the insecticidal activity of the novel formulated mixture exhibited two to three times the insecticidal activity of the individual insecticidal compounds.

Adult Colorado potato beetle insecticidal activity data at selected rates of application in which the technical active ingredients were not formulated but were dissolved as described above are provided in Table 4. The bold and italicized

numbers indicate that a beneficial insecticidal effect was observed when compared to the individual compounds.

Table 4
Adult Colorado potato beetle (*Leptinotarsa decemlineata* [Say]) Insecticidal Activity of Bifenthrin and Cyano-pyrethroids

5

Cyano Pyrethroid	Rate of Application (ppm)	% Mortality Adult Colorado Potato Beetle			
		bifenthrin			
		Rate of Application(ppm)			
		0	0.3	1.0	3.0
cyfluthrin	0	0	0	0	80
	0.3	10	0	10	60
	1.0	70	70	70	90
	3.0	80	80	100	100
	10.0	100	100	100	100
lambda-cyhalothrin	0	0	0	0	80
	0.3	30	50	70	100
	1.0	100	90	100	100
	3.0	100	100	100	100
	10.0	100	100	100	100
delta-methrin	0	0	0	0	10
	0.3	0	0	0	0
	1.0	30	60	60	30
	3.0	90	100	90	80
	10.0	100	100	100	100
esfenvalerate^a	0	0	0	10	70
	0.3	0	0	20	40
	1.0	0	0	10	35
	3.0	5	60	55	45
	10.0	95	85	100	95
alpha-cypermethrin	0	0	0	0	10
	0.3	30	0	0	20
	1.0	70	30	10	100
	3.0	100	70	NT	100
	10.0	100	90	100	100

a. % mortality for esfenvalerate and bifenthrin is the average of two tests.

Corn earworm insecticidal activity data at selected rates of application in which the technical active ingredients were dissolved as described above are provided in Table 5. The bold and italicized numbers indicate that a beneficial insecticidal effect was observed when compared to the individual compounds.

5

Table 5
Corn Earworm (*Heliothis zea* [Boddie]) Insecticidal Activity of Bifenthrin and Cyano-pyrethroids

Cyano Pyrethroid	Rate of Application (ppm)	% Mortality Corn Earworm			
		bifenthrin			
		Rate of Application (ppm)			
		0.0	0.1	0.3	1.0
cyfluthrin	0	6	NT	13	100
	0.3	13	NT	31	63
	1.0	69	NT	88	100
	3.0	100	NT	100	100
	10.0	100	NT	100	100
lambda-cyhalothrin	0	0	6	13	75
	0.3	6	0	13	75
	1.0	31	19	56	100
	3.0	56	75	94	100
	10.0	100	94	100	100
delta-methrin	0	0	6	13	75
	0.3	6	13	38	94
	1.0	50	56	75	100
	3.0	94	100	100	100
	10.0	100	100	100	100
esfenvalerate	0	0	6	13	75
	0.3	0	0	0	82
	1.0	0	13	13	67
	3.0	13	19	62	100
	10.0	50	88	75	100
alpha-cypermethrin	0	0	6	25	63
	0.3	6	12	75	100
	1.0	63	38	63	100

Cyano Pyrethroid	Rate of Application (ppm)	% Mortality Corn Earworm			
		bifenthrin			
		Rate of Application (ppm)			
		0.0	0.1	0.3	1.0
	3.0	100	94	100	100
	10.0	100	100	100	100

5 Cotton aphid insecticidal activity data at selected rates of application in which the technical active ingredients were dissolved as described above are provided in Table 6. The bold and italicized numbers indicate that a beneficial insecticidal effect was observed when compared to the individual compounds.

Table 6
Cotton Aphid (*Aphis gossypii* [Glover]) Insecticidal Activity of Bifenthrin and Cyano-pyrethroids

10

Cyano Pyrethroid	Rate of Application (ppm)	% Mortality Cotton Aphid			
		bifenthrin			
		Rate of Application (ppm)			
		0	30.0	100.0	200.0
cyfluthrin	0	4	15	30	NT*
	10.0	4	8	58	NT
	30.0	6	13	78	NT
	100.0	9	3	56	NT
lambda-cyhalothrin	0	4	15	30	NT
	10.0	11	22	53	NT
	30.0	11	15	71	NT
	100.0	10	45	80	NT
delta-methrin	0	2	35	88	100
	30.0	7	11	46	55
	100.0	8	33	63	90
	200.0	19	42	63	100
Esfenvalerate ^a	0	5	34	94	100
	30.0	38	41	93	91
	100.0	14	45	92	100
	200.0	15	32	97	93

Cyano Pyrethroid	Rate of Application (ppm)	% Mortality Cotton Aphid			
		bifenthrin			
		Rate of Application (ppm)			
		0	30.0	100.0	200.0
alpha-cypermethrin	0	6	17	100	100
	30.0	7	16	70	69
	100.0	3	10	43	100
	200.0	7	19	50	92

* NT = Not Tested

a. % mortality for esfenvalerate and bifenthrin is the average of two tests.

5 Twospotted spider miticidal activity data at selected rates of application in which the technical active ingredients were dissolved as described above are provided in Table 7. The bold and italicized numbers indicate that a beneficial insecticidal effect was observed when compared to the individual compounds.

Table 7

10 Twospotted Spider Mite (*Tetranychus urticae* [Koch]) Insecticidal Activity of Bifenthrin and Cyano-pyrethroids

Cyano Pyrethroid	Rate of Application (ppm)	% Mortality Twospotted Spider Mite				
		bifenthrin				
		Rate of Application (ppm)				
		0	10.0	30.0	60.0	100.0
cyfluthrin	0	1	20	66	68	75
	10.0	14	5	24	79	57
	30.0	17	4	46	66	97
	60.0	23	10	100	95	100
	100.0	11	96	42	100	91
lambda-cyhalothrin	0	1	20	66	68	75
	10.0	16	5	83	96	84
	30.0	19	20	95	85	94
	60.0	55	68	100	96	96
	100.0	39	78	93	95	97
delta-methrin	0	12	9	100	NT*	90
	10.0	3	95	100	NT	100

Cyano Pyrethroid	Rate of Application (ppm)	% Mortality Twospotted Spider Mite				
		bifenthrin				
		Rate of Application (ppm)				
		0	10.0	30.0	60.0	100.0
	30.0	83	100	100	NT	100
	100.0	26	100	97	NT	100
	200.0	16	94	100	NT	100
esfenvalerate	0	12	9	100	NT	90
	10.0	21	35	100	NT	97
	30.0	25	18	98	NT	99
	100.0	71	60	95	NT	100
	200.0	91	98	94	NT	98
alpha- cypermethrin	0	4	16	69	NT	100
	10.0	8	23	80	NT	95
	30.0	8	31	87	NT	100
	100.0	16	57	94	NT	91
	200.0	32	46	94	NT	90

* NT = Not Tested

5 While this invention has been described with an emphasis upon preferred embodiments, it will be understood by those of ordinary skill in the art that variations of the preferred embodiments may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the following claims.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

- 2006330918 15 Dec 2011
1. A miticidal composition including bifenthrin and a cyano-pyrethroid selected from the group consisting of deltamethrin, cyfluthrin, *alpha*-cypermethrin, *zeta*-cypermethrin, *lambda*-cyhalothrin, and esfenvalerate, wherein the weight ratio of bifenthrin to cyano-pyrethroid is from 10:1 to 1:30.
5
 2. A composition of claim 1 wherein the cyano-pyrethroid is *zeta*-cypermethrin.
 3. A composition of claim 2 wherein the *zeta*-cypermethrin is (R,S)- α -cyano-3-phenoxybenzyl-(1RS)-*cis-trans*-3-(2,2-dichlorovinyl)-2,2-
10 dimethylcyclopropanecarboxylate which has been enriched in the 1R-*cis*-S and 1R-*trans*-S isomers by the reaction of a 55/45 *cis/trans* mixture of cypermethrin with a catalytic amount of tricapyrylammonium chloride and sodium carbonate in n-heptane.
 4. A composition of claim 1 further including an agriculturally acceptable
15 extender or adjuvant.
 5. The composition of claim 1 wherein the weight ratio of bifenthrin to cyano-pyrethroid is from 4:1 to 1:4.
 6. The composition of claim 5 wherein the weight ratio of bifenthrin to cyano-pyrethroid is from 3:1 to 1:3.
 - 20 7. The composition of claim 5 wherein the cyano-pyrethroid is *zeta*-cypermethrin.
 8. A method for controlling unwanted insects or mites including applying a composition of claim 1 to the foliar portion of a plant.
 9. The method of claim 8 wherein the weight ratio of bifenthrin to cyano-
25 pyrethroid is from 4:1 to 1:4.

10. The method of claim 9 wherein the cyano-pyrethroid is *zeta*-cypermethrin.

11. A foliar insecticidal or miticidal composition including bifenthrin and a cyano-pyrethroid selected from the group consisting of deltamethrin, cyfluthrin, *alpha*-cypermethrin, *zeta*-cypermethrin, *lambda*-cyhalothrin, and esfenvalerate,
5 wherein the weight ratio of bifenthrin to cyano-pyrethroid is from 10:1 to 1 :30.

12. The composition of claim 11 wherein the weight ratio of bifenthrin to cyano-pyrethroid is from 4:1 to 1:4.

13. The composition of claim 12 wherein the weight ratio of bifenthrin to cyano-pyrethroid is from 3:1 to 1:3.

10 14. The composition of claim 12 wherein the cyano-pyrethroid is *zeta*-cypermethrin.

15 15. The composition of claim 14 wherein the *zeta*-cypermethrin is (R,S)- α -cyano-3-phenoxybenzyl-(1RS)-*cis-trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate which has been enriched in the 1R-*cis*-S and
15 1R-*trans*-S isomers by the reaction of a 55/45 *cis/trans* mixture of cypermethrin with a catalytic amount of tricapyrylammonium chloride and sodium carbonate in n-heptane.

16. The composition of claim 11 further including an agriculturally acceptable extender or adjuvant.

20 17. A miticidal composition substantially as described herein.

18. A method for controlling unwanted insects or mites substantially as described herein.

19. A foliar insecticidal or miticidal composition substantially as described herein.

FMC CORPORATION

WATERMARK PATENT & TRADE MARK ATTORNEYS

P30553AU00

2006330918 15 Dec 2011