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(71) Applicant: **WILLOWOOD CHEMICALS PRIVATE LIMITED** [IN/IN]; 409, Fourth Floor, Salcon Aurum, District Centre, Jasola, New Delhi –110025, (IN).

(72) Inventors: **MUNDHRA, Parikshit**; 409, Fourth Floor, Salcon Aurum, District Centre, Jasola, New Delhi -110025 (IN). **MOHAN, Jitendra**; 409, Fourth Floor, Salcon Aurum, District Centre, Jasola, New Delhi -110025 (IN).

(74) Agent: **SINGH, Hemant**; Inttl Advocare, F-252, Lane W/5, Western Avenue, Sainik Farms, New Delhi – 110062 (IN).

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(54) Title: SYNERGISTIC INSECTICIDAL COMPOSITIONS

(57) Abstract: The present invention relates to a synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate and any one of pymetrozine, flubendiamide, deltamethrin and lambda-cyhalothrin. The composition of the present invention decreases application rates of each of the active ingredients and is non-phytotoxic.

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SYNERGISTIC INSECTICIDAL COMPOSITIONS

FIELD OF THE INVENTION

The present invention relates to synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate and any one of pymetrozine, flubendiamide, deltamethrin and lambda-cyhalothrin. The present invention also relates to process for preparing said composition.

BACKGROUND OF THE INVENTION

Insects are very destructive to crops and can result in significant loss of crop yield and quality, which results in economic loss to the grower and increased costs to the consumer. Insecticide compositions that can be applied at as low dose as possible and be effective in controlling pest species of insects while causing as little harm as possible to beneficial insects and minimal disturbance in the environment are in demand by the farming community.

Many insecticides are known and their insecticidal properties have been reported in various patents, by way of example, acephate in US 3845172, alanycarb in US 4444786, methoxyfenozide in US5344958, indoxacarb in US 5462938, deltamethrin in GB 1413491, fenpropathrin in GB 1356087, lambda-cyhalothrin in EP 106469, chlorpyrifos in US 3244586, profenofos GB 1417116, quinalphos in DE 1545817, triazophos DE 1670876, acetamiprid in US 5304566, imidacloprid in EP 0192060, novaluron in US 4980376, lufenuron in US 4798837, chlorantraniliprole in US 6747047, cyantraniliprole in US 6747047, flubendiamide in US 6603044, spinosad in US 5202242 and diafenthiuron in GB 2060626.

Combinations of two or more insecticides are also known and have been reported in various patents/patent applications. Chinese patent application CN 101919386 discloses an insecticidal composition containing methoxyfenozide and synthetic pyrethroid insecticide selected from etofenprox, bifenthrin or lambda-cyhalothrin.

Chinese patent application CN104705337 provides a pesticide composition comprising bifenthrin and indoxacarb wherein the mass ratio of bifenthrin to

indoxacarb is 1:40-40:1. Chinese patent application CN103518765 discloses a combination of indoxacarb and methoxyfenozide in that the weight ratio of the indoxacarb and methoxyfenozide is 2% - 50%.

Indian patent application IN201621027690 discloses comprising A) methoxyfenozide B) at least one insecticide selected from indoxacarb and emamectin benzoate C) at least one more insecticide selected from bifenthrin, cypermethrin, deltamethrin, fenpropathrin, lambda-cyhalothrin, acephate, chlorpyrifos, profenofos, quinalphos, triazophos, acetamiprid, clothianidin, imidacloprid, thiamethoxam, novaluron, lufenuron, chlorfluazuron, pyriproxyfen, chlorantraniliprole, cyantraniliprole, flubendiamide, abamectin, spinetoram, spinosad, chlorfenapyr, diafenthiuron, fipronil, pyridalyl and tolfenpyrad with one or more inactive excipients. The following combinations are illustrated: methoxyfenozide 20% + indoxacarb 7.5% + bifenthrin 5%; methoxyfenozide 14% + indoxacarb 5% + profenofos 20%; methoxyfenozide 20% + emamectin benzoate 7.5% + bifenthrin 5%; methoxyfenozide 20% + emamectin benzoate 7.5% + profenfos 5%; methoxyfenozide 20% + emamectin benzoate 7.5% + thiamethoxam 5%.

Indian patent application 201821023081 discloses the following combinations of insecticides: pymetrozine 25% + flupyrimin 10% + thiamethoxam 10%, pymetrozine 25%+ flupyrimin 10% + chlorantraniliprole 6%, pymetrozine 25% + triflumezopyrim 4% + chlorantraniliprole 6%, pymetrozine 15.63% + triflumezopyrim 2.5% + thiamethoxam 6.25%, pymetrozine 12.5% + flupyrimin 5% + thiamethoxam 5%, pymetrozine 12.5% + flupyrimin 5% + tolfenpyrad 7.5%, pymetrozine 12.5% + triflumezopyrim 2% + tolfenpyrad 7.5%.

It is believed that by combining different insecticides, it is sometimes possible to attain one or more of the following advantages: broaden the spectrum of insect control, minimize the doses of chemicals use, retard resistance development and reduce the cost of treatment.

However, not all combinations provide the expected advantages and hence, there still exists a need to provide novel insecticidal compositions that exhibit

synergistically enhanced action, have a broader scope of activity, reduced cost of treatment and overcomes the development of resistance due to the repeated use of the known combinations.

SUMMARY OF THE INVENTION

The inventors of the present invention have surprisingly found that a combination of methoxyfenozide, emamectin benzoate and any one of pymetrozine, flubendiamide, deltamethrin and lambda-cyhalothrin provides enhanced synergistic insecticidal activity.

Accordingly, the present invention provides a synergistic insecticidal composition comprising: a) 15 to 25%w/w of methoxyfenozide; b) 0.1 to 3%w/w of emamectin benzoate; c) 0.5 to 20%w/w of one of pymetrozine, flubendiamide, deltamethrin, and lambda-cyhalothrin; and d) at least one excipient.

In an embodiment the composition of the present invention, comprises 21% w/w of methoxyfenozide, 1.1%w/w of emamectin benzoate and 15% w/w of pymetrozine.

In another embodiment the composition of the present invention, comprises 21% w/w of methoxyfenozide, 1.1%w/w of emamectin benzoate and 3.5% w/w of flubendiamide.

In yet another embodiment the composition of the present invention, comprises 21% w/w of methoxyfenozide, 1.1%w/w of emamectin benzoate and 1.25%w/w of deltamethrin.

In one another embodiment the composition of the present invention, comprises 21% w/w of methoxyfenozide, 1.1%w/w of emamectin benzoate and 1.5%w/w of lambda-cyhalothrin.

In another embodiment, the composition is formulated as Capsule suspension (CS), Dispersible concentrate (DC), Dustable powder (DP), Powder for dry seed treatment (DS), Emulsifiable concentrate (EC), Emulsifiable granule (EG), Emulsion water-in-oil (EO), Emulsifiable powder (EP), Emulsion for seed treatment (ES), Emulsion oil-in-water (EW), Flowable concentrate for seed

treatment (FS), Granules (GR), Micro-emulsion (ME), Oil-dispersion (OD), Oil miscible flowable concentrate (OF), Oil miscible liquid (OL), Oil dispersible powder (OP), Suspension concentrate (SC), Suspension concentrate for direct application (SD), Suspo-emulsion (SE), Water soluble granule (SG), Soluble concentrate (SL), Spreading oil (SO), Water soluble powder (SP), Water soluble tablet (ST), Ultra-low volume (ULV) suspension, Tablet (TB), Ultra-low volume (ULV) liquid, Water dispersible granules (WG), Wettable powder (WP), Water dispersible powder for slurry seed treatment (WS), Water dispersible tablet (WT), a mixed formulation of CS and SC (ZC) or A mixed formulation of CS and SE (ZE), a mixed formulation of CS and EW (ZW). In a preferred embodiment the composition is formulated as suspension concentrate.

In an embodiment the composition of the present invention comprises excipient selected from the group comprising dispersing agent, wetting agent, anti-freezing agent, defoamer, biocide and thickener.

In yet another embodiment, the dispersing agent is selected from the group comprising amine salt of phosphate tristyryl phenol ethoxylated, acrylic copolymer, graft copolymer and combinations thereof, and present in an amount in the range from 2 to 10% w/w.

In one another embodiment, the wetting agent is selected from the group comprising ethoxylated polyarylphenol phosphate ester, dioctyl sulphosuccinate, non-ionic ethoxylate and combinations thereof, and present in an amount in the range from 1 to 5% w/w.

In an embodiment, the anti-freezing agent is selected from the group comprising propylene glycol, diethylene glycol, monoethylene glycol and combinations thereof, and present in an amount in the range from 2 to 10% w/w.

In another embodiment, the defoamer is dimethyl polysiloxane emulsion and present in an amount in the range from 0.01 to 0.5% w/w.

In one another embodiment, the biocide is selected from the group consisting of 20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one,

formaldehyde and combinations thereof and present in an amount in the range from 0.01 to 0.50% w/w.

In another embodiment, the thickener is xanthan gum and is present in an amount in the range from 0.01 to 0.50% w/w.

DETAILED DESCRIPTION OF THE INVENTION

Discussed below are some representative embodiments of the present invention. The invention in its broader aspects is not limited to the specific details and representative methods. The illustrative examples are described in this section in connection with the embodiments and methods provided. The invention according to its various aspects is particularly pointed out and distinctly claimed in the appended claims read in view of this specification and appropriate equivalents.

It is to be noted that, as used in the specification and the appended claims, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a composition containing “a compound” includes a mixture of two or more compounds. It should also be noted that the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

The expression of various quantities in terms of “% w/w” or “%” means the percentage by weight, relative to the weight of the total solution or composition unless otherwise specified.

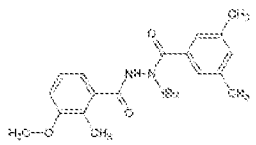
The term “active ingredient” (A.I.) or “active agent” used herein refers to that component of the composition responsible for control of insect-pests.

As used herein, the expressions “SL formulation”, “SC formulation” “WDG or WG formulation” “GR formulation”, “DF formulation”, “CG formulation”, “EC formulation”, “EW formulation”, “ME formulation”, “WP formulation” are the international denominations adopted by the FAO (Food and Agricultural Organization of the United Nations) to designate “soluble liquid”, “aqueous suspension concentrate”, “water dispersible granules”, “granular”, “dry flowable”,

"capsulated granules", "emulsion concentrate", "emulsion", "micro-emulsion" and "wettable powder" respectively.

In accordance with an embodiment of the invention, there is provided a synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate and any one of pymetrozine, flubendiamide, deltamethrin and lambda-cyhalothrin.

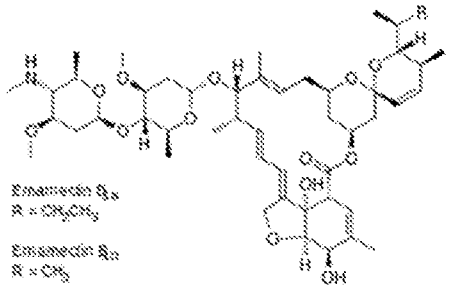
Methoxyfenozide (IUPAC name: N-tert-butyl-N′-(3-methoxy-o-toluoyl)-3,5-xylohydrazide) belongs to the class of diacylhydrazine insecticides and is represented by following structure:



It is an agonist of the hormone 20-hydroxyecdysone. Methoxyfenozide causes cessation of feeding and premature lethal moult. It lethally accelerates the moulting process. It is active primarily by ingestion, also with some contact and ovicidal activity. It does not have translaminar or phloem-systemic properties. It provides effective control of Lepidoptera. Example target pests include *Spodoptera, Pieris, Colias, Mamestra, Hellula, Manduca, Autographa, Trichoplusia, Plusia, Rachiplusia, Pseudaletia, Pseudoplusia, Anticarsia, Diaphania, Ostrinia, Alabama, Diatraea, Epinotia, Keiferia, Cnaphalocrocis, Cydia, Capua, Choristoneura, Adoxophyes, Epiphyas, Archips, Argyrotaenia, Lithophane, Pandemis, Acrobasis, Platynota, Lobesia, Desmia, Clysia, Endopiza, Harrisina, Sparganothis spp.*

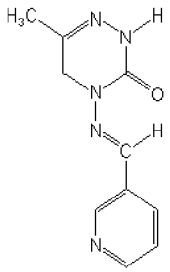
Emamectin benzoate (IUPAC name: A mixture containing 90% of (10E,14E,16E)-(1R,4S,5′S,6S,6′R,8R,12S,13S,20R,21R,24S)-6′-[(S)-sec-butyl]-21,24-dihydroxy-5′,11,13,22-tetramethyl-2-oxo-(3,7,19-trioxatetracyclo[15.6.1.14,8.020,24]pentacosa-10,14,16,22-tetraene-6-spiro-2′-

(5′,6′-dihydro-2′H-pyran)-12-yl 2,6-dideoxy-3-O-methyl-4-O-(2,4,6-trideoxy-3-O-methyl-4-methylamino-α-L-lyxo-hexopyranosyl)-α-L-arabino-hexopyranoside benzoate and 10% of (10E,14E,16E)-(1R,4S,5′S,6S,6′R,8R,12S,13S,20R,21R,24S)-21,24-dihydroxy-6′-isopropyl-5′,11,13,22-tetramethyl-2-oxo-3,7,19-trioxatetracyclo[15.6.1.14,8.020,24]pentacosa-10,14,16,22-tetraene-6-spiro-2′-(5′,6′-dihydro-2′H-pyran)-12-yl 2,6-dideoxy-3-O-methyl-4-O-(2,4,6-trideoxy-3-O-methyl-4-methylamino-α-L-lyxo-hexopyranosyl)-α-L-arabino-hexopyranoside benzoate) belongs to the class of avermectin insecticides and is represented by following structure:



It is a produced by bacterium Streptomyces avermitilis and is effective against many insect pests. It acts by stimulating the release of gamma-aminobutyric acid, an inhibitory neurotransmitter, thus finally activating chloride channels. It is a non-systemic insecticide which penetrates leaf tissues by translaminar movement.

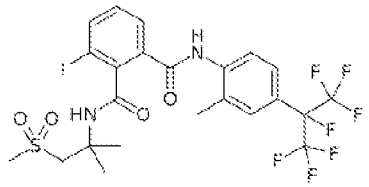
Pymetrozine is a pyridine azomethine insecticide and is represented by the following structural formula-



IUPAC: (E)-4,5-dihydro-6-methyl-4-(3-pyridylmethyleneamino)-1,2,4-triazin-3(2H)-one

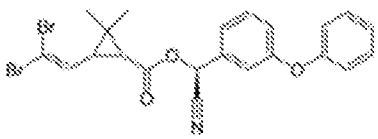
Pymetrozine is selective against Homoptera, causing them to stop feeding. It provides control of juvenile and adult stages of aphids and whiteflies in vegetables, potatoes, ornamental, cotton, deciduous fruit, citrus, tobacco and hops and planthoppers in rice.

Flubendiamide (IUPAC name: 3-iodo-N'-~~2~~(2-mesyl-1,1-dimethylethyl)-N-{4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]-o-tolyl}phthalamide) belongs to the class of diamide insecticides and is represented by the following structure:



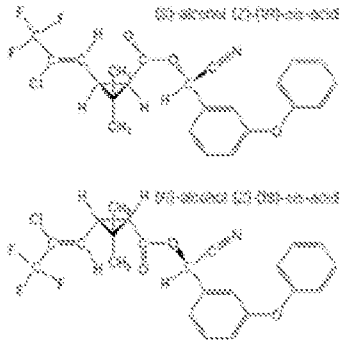
Flubendiamide activates the ryanodine receptor, a calcium release channel which is involved in muscle contraction. It is activated by ingestion. It is used for control of both adult and larval lepidopterous insects in maize, cotton, tobacco, pome and stone fruit, nuts, grapes, rice, turf and vegetables.

Deltamethrin (IUPAC name: (S)-α-cyano-3-phenoxybenzyl (1R,3R)-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate; Roth: (S)-α-cyano-3-phenoxybenzyl (1R)-cis-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate) belongs to pyrethroid group of insecticides. It is represented by the following structure:



It is a non-systemic insecticide with contact and stomach action. It prevents the sodium channels from functioning, so that no transmission of nerve impulses can take place.

Lambda-cyhalothrin (IUPAC name: Mixture of (R)-α-cyano-3-phenoxybenzyl (1S,3S)-3-[(Z)-2-chloro-3,3,3-trifluoropropenyl]-2,2-dimethylcyclopropanecarboxylate and (S)-α-cyano-3-phenoxybenzyl (1R,3R)-3-[(Z)-2-chloro-3,3,3-trifluoropropenyl]-2,2-dimethylcyclopropanecarboxylate; Roth: Mixture of (R)-α-cyano-3-phenoxybenzyl (1S)-cis-3-[(Z)-2-chloro-3,3,3-trifluoropropenyl]-2,2-dimethylcyclopropanecarboxylate and (S)-α-cyano-3-phenoxybenzyl (1R)-cis-3-[(Z)-2-chloro-3,3,3-trifluoropropenyl]-2,2-dimethylcyclopropanecarboxylate) belongs to pyrethroid class of insecticides. It is represented by following structure.



It is a non-systemic insecticide with contact and stomach action, and repellent properties. It acts on the nervous system of insects and disturbs the function of neurons by interaction with sodium channel.

The present invention provides a synergistic insecticidal composition comprising:

15 to 25%w/w of methoxyfenozide; 0.1 to 3%w/w of emamectin benzoate; 0.5 to 20%w/w of one of pymetrozine, flubendiamide, deltamethrin, and lambda-cyhalothrin; and at least one excipient.

In an aspect, methoxyfenozide is present in an amount from 15 to 25% w/w, emamectin benzoate is present in an amount from 0.1 to 3%w/w and pymetrozine is present in an amount from 10 to 20% w/w. Preferably, methoxyfenozide is present in an amount of 21% w/w, emamectin benzoate is present in an amount of 1.1% w/w and pymetrozine is present in an amount of 15%w/w.

In another aspect, methoxyfenozide is present in an amount from 15 to 25% w/w, emamectin benzoate is present in an amount from 0.1 to 3% w/w and flubendiamide is present in an amount from 2.5 to 5% w/w. Preferably, methoxyfenozide is present in an amount of 21% w/w, emamectin benzoate is present in an amount of 1.1% w/w and flubendiamide is present in an amount of 3.5%w/w.

In another aspect, methoxyfenozide is present in an amount from 15 to 25% w/w, emamectin benzoate is present in an amount from 0.1 to 3% w/w and deltamethrin is present in an amount from 0.5 to 2% w/w. Preferably, methoxyfenozide is present in an amount of 21% w/w, emamectin benzoate is present in an amount of 1.1% w/w and deltamethrin is present in an amount of 1.25%w/w.

In one another aspect, methoxyfenozide is present in an amount from 15 to 25% w/w, emamectin benzoate is present in an amount from 0.1 to 3% w/w and lambda-cyhalothrin. is present in an amount from 1 to 3%% w/w. Preferably, methoxyfenozide is present in an amount of 21% w/w, emamectin benzoate is present in an amount of 1.1% w/w and lambda-cyhalothrin is present in an amount of 1.5%w/w.

The excipients of the synergistic insecticidal composition of the present invention is selected from the group comprising dispersing agent, wetting agent, anti-freezing agent, defoamer, biocide, and thickener. All the excipients are agro-chemically acceptable and are obtained from commercial sources.

The synergistic composition of the present invention may be formulated as Capsule suspension (CS), Dispersible concentrate (DC), Dustable powder (DP), Powder for dry seed treatment (DS), Emulsifiable concentrate (EC), Emulsifiable granule (EG), Emulsion water-in-oil (EO), Emulsifiable powder (EP), Emulsion for seed treatment (ES), Emulsion oil-in-water (EW), Flowable concentrate for seed treatment (FS), Granules (GR), Micro-emulsion (ME), Oil-dispersion (OD), Oil miscible flowable concentrate (OF), Oil miscible liquid (OL), Oil dispersible powder (OP), Suspension concentrate (SC), Suspension concentrate for direct application (SD), Suspo-emulsion (SE), Water soluble granule (SG), Soluble

concentrate (SL), Spreading oil (SO), Water soluble powder (SP), Water soluble tablet (ST), Ultra-low volume (ULV) suspension, Tablet (TB), Ultra-low volume (ULV) liquid, Water dispersible granules (WG), Wettable powder (WP), Water dispersible powder for slurry seed treatment (WS), Water dispersible tablet (WT), a mixed formulation of CS and SC (ZC), a mixed formulation of CS and SE (ZE), a mixed formulation of CS and EW (ZW). The abbreviations provided for various formulations are the international denominations adopted by the FAO (Food and Agricultural Organization of the United Nations).

Preferably, the composition of the present invention is formulated as suspension concentrate.

The term "suspension concentrate" used herein refers to a suspension of the active insecticide and excipients in a small quantity of liquid, usually water.

It is generally observed that solid particles in a liquid undergo spontaneous aggregation to form lumps. Hence it is recommended to add a dispersing agent which prevents agglomeration of solid particles and keep them suspended in fluid. Accordingly, the composition of the present invention contains dispersing agents such as amine salt of phosphate tristyryl phenol ethoxylated, acrylic copolymer, graft copolymer, naphthalene sulphonate of formaldehyde condensate, acrylic copolymer, lignin based sulphonate. One or more dispersing agents may be used in the synergistic composition of the present invention. The dispersing agent is present in an amount in the range from 2 to 10% w/w.

Wetting is the first stage of dispersion, in which air surrounding the granular composition is substituted with water. Wetting of the composition with water cannot occur if the surface tension of the liquid is very high. Hence, it is recommended to add a wetting agent to the composition to facilitate the process of dispersion of the granules in the liquid. Non-limiting examples of wetting agents that can be used in the present invention include ethoxylated polyarylphenol phosphate ester, dioctyl sulphosuccinate, non-ionic ethoxylate, dioctyl sulfosuccinate, sodium lauryl sulfate, naphthalene alkyl aryl sulphonate. The alkyl aryl sulphonates in which the alkyl group contains approximately 1 to 5

carbon atoms and in which the aryl nucleus is selected from the group consisting of benzene and naphthalene. One or more wetting agents may be used in the synergistic composition of the present invention. The wetting agent is present in an amount in the range from 1 to 5% w/w.

An anti-freezing agent is generally added to the composition, to prevent the aqueous compositions from freezing. Suitable anti-freezing agents useful herein, but not limited to, include propylene glycol, diethylene glycol, monoethylene glycol and combinations thereof. Preferably, the anti-freezing agent is present in an amount in the range from 2 to 10% w/w.

A defoamer, also called as anti-foaming agent, is generally added to the composition as foam formation prevents the efficient filling of a container. Preferably, the defoamer is polydimethyl siloxane emulsion. In the insecticidal composition of the present invention the defoamer is present in an amount in the range from 0.01 to 0.5% w/w.

The synergistic insecticidal composition comprises a biocide selected from the group consisting of 20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one, formaldehyde and combinations thereof, and present in an amount in the range from 0.01 to 0.50% w/w. The biocide is added to the composition of the present invention for its preservation against spoilage from bacteria, yeasts and fungi.

It is necessary to add a thickener to the composition to reduce the tendency of the composition to disperse when sprayed, and decrease the likelihood of it being rinsed off from the crops. Preferably, the synergistic insecticidal composition comprises xanthan gum as thickener in an amount in the range from 0.01 to 0.50% w/w. Xanthan gum used in the present invention is obtained from commercial source.

The synergistic composition of the present invention is used to control wide variety of insects, by way of example, *Helicoverpa armigera*, pink bollworm, *Spodoptera litura*, lepidoptera, coleoptera, heteroptera, homoptera, thysanoptera,

acrididae, locusts, aphids, colorado beetles, thrips, jassids and whitefly in vegetables, brassicas, fruit, maize, tea, grapes, cotton, cereals, citrus, oilseed rape, soybeans and other crops.

In another aspect, the present invention provides a process for the preparation of suspension concentrate formulation comprising the synergistic composition. Alternatively, the formulation may be prepared by any method known in the art.

The inventors of the present invention have surprisingly found that a composition of the present invention is synergetic in nature. The synergetic composition of the present invention is more effective than their individual counterparts or when two actives are taken together. The synergetic composition of the present invention also makes it possible to use markedly smaller quantities of the active ingredients as compared to their individual counterparts.

The composition of the present invention is effective in controlling wide spectrum of insect pests, delays the emergence of the resistant strains of the insect-pests and achieves effective and economic control of undesired insect-pests. The composition of the present invention is relatively safer to human beings, animals and is non-phytotoxic.

The synergistic composition of the present invention provides a number of other advantages-

- Increased efficacy in comparison to the other formulations tested during the trials.
- Economically beneficial to the farmers as it provides better yield of the crop with reduction in the number of sprays
- Reduced possibility of hazards to the farmers due to occupational exposure because of reduction in the number of sprays and
- Is storage stable

The embodiments of the present invention are more particularly described in the following examples that are intended as illustrations only, since numerous

modifications and variations within the scope of the present invention will be apparent to those of skill in the art. Unless otherwise noted, all parts, percentages and ratios reported in the following examples are on a weight basis and all reagents used in the examples were obtained or are available from the chemical suppliers.

EXAMPLES

The synergistic insecticidal composition of the present invention comprising methoxyfenozide, emamectin benzoate and pymetrozine in the form of suspension concentrate is provided in Table 1. The unit of each component of the composition are expressed in "% w/w" i.e. the percentage by weight, relative to the weight of the total solution or composition.

Table 1: Synergistic insecticidal composition comprising Methoxyfenozide, Emamectin Benzoate, Pymetrozine in suspension concentrate (SC) form

S. No.	Component	Function	Quantity (% w/w)
1	Methoxyfenozide	Active ingredient	21
2	Emamectin Benzoate	Active ingredient	1.1
3	Pymetrozine	Active ingredient	15
4	Propylene glycol/Diethylene glycol/Monoethylene glycol	Anti-freezing agent	2-10
5	Amine salt of phosphate tristyryl phenol ethoxylated/Acrylic copolymer Graft polymer	Dispersing agent	2-10
6	Ethoxylated polyaryl phenol phosphate ester/ Non-ionic ethoxylate/ Dioctyl sulphosuccinate	Wetting agent	1-5

7	Dimethyl Polysiloxane emulsion	Defoamer	0.01-0.5
8	20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one/ Formaldehyde	Biocide	0.01-0.5
9	Xanthan Gum	Thickener	0.01-0.5
10	Demineralised water	Solvent	Q.S

QS: quantity sufficient required to make 100% w/w formulation

Table 2 provides quantities of active ingredients and raw material charged to prepare the synergistic composition of the present invention in SC form. The active ingredients are in technical grade. The entries for active ingredients, in table 2 varies from that of table 1, as the entries in table 1 are for 100% pure compounds whereas the entries in Table 2 are for technical ones with certain percentage of impurities. Hence, methoxyfenozide 21% w/w, emamectin benzoate 1.1% w/w, pymetrozine 15% w/w of 100% purity of Table 1 corresponds to methoxyfenozide 21.32g of 98.5% purity, emamectin benzoate 1.16g and pymetrozine 15.8g of 95% purity each, of Table 2.

Table 2: Quantities of active ingredients and raw material charged

S. No.	Components	Amount (g)
1	Methoxyfenozide Technical (Basis of 98.5%)	21.32
2	Emamectin Benzoate Technical (Basis of 95%)	1.16
3	Pymetrozine Technical (Basis of 95%)	15.80
4	Propylene glycol	5.00

5	Graft copolymer	5.00
6	Non-ionic ethoxylate	3.00
7	Dimethyl Polysiloxane emulsion	0.10
8	20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one	0.10
9	Xanthan gum	0.10
10	Demineralised water	48.42

Example 1: Process of preparing synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate and pymetrozine in suspension concentrate (SC) form

All the components were weighed as per table 2. The graft copolymer (5g) and non-ionic ethoxylate (3g) were diluted in demineralised water and solubilized by high shear mixing. Then propylene glycol (5g), methoxyfenozide (21.32g), emamectin benzoate (1.16g), pymetrozine (15.80 g), dimethyl polysiloxane emulsion (0.10 g), 20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one (0.10g) were added and mixed to obtain a homogeneous mass. The homogeneous mass was grinded in bead mill. The grinding was carried out until a mean particle size of 3-5(D-90) microns was obtained. After grinding, 2% water solution of xanthan gum was added under low stirring to obtain the title insecticidal composition.

Table 3: Synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate, flubendiamide in suspension concentrate (SC) form

S. No.	Component	Function	Quantity (% w/w)
1	Methoxyfenozide	Active ingredient	21

2	Emamectin Benzoate	Active ingredient	1.1
3	Flubendiamide	Active ingredient	3.5
4	Propylene glycol/Diethylene glycol/Monoethylene glycol	Anti-freezing agent	2-10
5	Amine salt of phosphate tristyryl phenol ethoxylated/Acrylic copolymer Graft polymer	Dispersing agent	2-10
6	Ethoxylated polyaryl phenol phosphate ester/ Non-ionic ethoxylate/ Dioctyl sulphosuccinate	Wetting agent	1-5
7	Dimethyl Polysiloxane emulsion	Defoamer	0.01-0.5
8	20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one/ Formaldehyde	Biocide	0.01-0.5
9	Xanthan Gum	Thickener	0.01-0.5
10	Demineralised water	Solvent	Q.S

QS: quantity sufficient required to make 100% w/w formulation

Table 4 provides quantities of active ingredients and raw material charged to prepare the synergistic composition of the present invention in SC form. The entries for active ingredients, in table 4 varies from that of table 3, as the entries in table 3 are for 100% pure compounds whereas the entries in Table 4 are for technical ones with certain percentage of impurities. Hence, methoxyfenozide 21% w/w, emamectin benzoate 1.1% w/w, flubendiamide 3.5% w/w of 100% purity of Table 1 corresponds to methoxyfenozide 21.32g of 98.5% purity, emamectin benzoate 1.16g and pymetrozine 15.8g of 95% purity each, of Table 4.

Table 4: Quantities of active ingredients and raw material charged

S.No	Components	Amount (g)
1	Methoxyfenozide Technical (Basis of 98.5%)	21.32
2	Emamectin Benzoate Technical (Basis of 95%)	1.16
3	Flubendiamide Technical (Basis of 95%)	3.70
4	Propylene glycol	5.00
5	Graft copolymer	5.00
6	Non-ionic ethoxylate	3.00
7	Dimethyl Polysiloxane emulsion	0.10
8	20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one	0.10
9	Xanthan gum	0.10
10	Demineralised water	60.52

Example 2: Process of preparing synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate and flubendiamide in suspension concentrate (SC) form

All the components were weighed as per table 2. The graft copolymer (5g) and non-ionic ethoxylate (3g) were diluted in demineralised water and solubilized by high shear mixing. Then propylene glycol (5g), methoxyfenozide (21.32g), emamectin benzoate (1.16g), flubendiamide (3.70g), dimethyl polysiloxane emulsion (0.10g), 20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one (0.10g) were added and mixed to obtain a homogeneous mass. The homogeneous mass was grinded in bead mill. The grinding was

carried out until a mean particle size of 3-5(D-90) microns was obtained. After grinding, 2% water solution of xanthan gum was added under low stirring to obtain the title insecticidal composition.

Table 5: Synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate, deltamethrin in suspension concentrate (SC) form

S. No.	Component	Function	Quantity (% w/w)
1	Methoxyfenozide	Active ingredient	21
2	Emamectin Benzoate	Active ingredient	1.1
3	Deltamethrin	Active ingredient	1.25
4	Propylene glycol/Diethylene glycol/Monoethylene glycol	Anti-freezing agent	2-10
5	Amine salt of phosphate tristyryl phenol ethoxylated/Acrylic copolymer Graft polymer	Dispersing agent	2-10
6	Ethoxylated polyaryl phenol phosphate ester/ Non-ionic ethoxylate/ Dioctyl sulphosuccinate	Wetting agent	1-5
7	Dimethyl Polysiloxane emulsion	Defoamer	0.01-0.5
8	20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one/ Formaldehyde	Biocide	0.01-0.5
9	Xanthan Gum	Thickener	0.01-0.5
10	Demineralised water	Solvent	Q.S

QS: quantity sufficient required to make 100% w/w formulation

Table 6 provides quantities of active ingredients and raw material charged to prepare the synergistic composition of the present invention in SC form. The active ingredients are in technical grade. The entries for active ingredients, in table 6 varies from that of table 5, as the entries in table 1 are for 100% pure compounds whereas the entries in Table 6 are for technical ones with certain percentage of impurities. Hence, methoxyfenozide 21% w/w, emamectin benzoate 1.1% w/w, deltamethrin 1.25% w/w of 100% purity of Table 1 corresponds to methoxyfenozide 21.32g of 98.5% purity, emamectin benzoate 1.16g of 95% purity and deltamethrin 1.28g of 98% purity, of Table 6.

Table 6: Quantities of active ingredients and raw material charged

S. No.	Components	Amount (g)
1	Methoxyfenozide Technical (Basis of 98.5%)	21.32
2	Emamectin Benzoate Technical (Basis of 95%)	1.16
3	Deltamethrin Technical (Basis of 98%)	1.28
4	Propylene glycol	5.00
5	Graft copolymer	5.00
6	Non-ionic ethoxylate	3.00
7	Dimethyl Polysiloxane emulsion	0.10
8	20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one	0.10
9	Xanthan gum	0.10
10	Demineralised water	62.94

Example 3: Process of preparing synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate and deltamethrin in suspension concentrate (SC) form

All the components were weighed as per table 6. The graft copolymer (5g) and non-ionic ethoxylate (3g) were diluted in demineralised water and solubilized by high shear mixing. Then propylene glycol (5g), methoxyfenozide (21.32g), emamectin benzoate (1.16g), deltamethrin (1.28 g), dimethyl polysiloxane emulsion (0.10g), 20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one (0.10g) were added and mixed to obtain a homogeneous mass. The homogeneous mass was grinded in bead mill. The grinding was carried out until a mean particle size of 3-5(D-90) microns was obtained. After grinding, 2% water solution of xanthan gum was added under low stirring to obtain the title insecticidal composition.

Table 7: Synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate, lambda-cyhalothrin in suspension concentrate (SC) form

S. No.	Component	Function	Quantity (% w/w)
1	Methoxyfenozide	Active ingredient	21
2	Emamectin Benzoate	Active ingredient	1.1
3	Lambda-cyhalothrin	Active ingredient	1.5
4	Propylene glycol/Diethylene glycol/Monoethylene glycol	Anti-freezing agent	2-10
5	Amine salt of phosphate tristyryl phenol ethoxylated/Acrylic copolymer Graft polymer	Dispersing agent	2-10
6	Ethoxylated polyaryl phenol phosphate ester/ Non-ionic	Wetting agent	1-5

	ethoxylate/ Dioctyl sulphosuccinate		
7	Dimethyl Polysiloxane emulsion	Defoamer	0.01-0.5
8	20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one/ Formaldehyde	Biocide	0.01-0.5
9	Xanthan Gum	Thickener	0.01-0.5
10	Demineralised water	Solvent	Q.S

QS: quantity sufficient required to make 100% w/w formulation

Table 8 provides quantities of active ingredients and raw material charged to prepare the synergistic composition of the present invention comprising methoxyfenozide, emamectin benzoate, lambda-cyhalothrin in SC form. The active ingredients are in technical grade. The entries for active ingredients, in table 8 varies from that of table 7, as the entries in table 7 are for 100% pure compounds whereas the entries in table 8 are for technical ones with certain percentage of impurities. Hence, methoxyfenozide 21% w/w, emamectin benzoate 1.1% w/w, lambda-cyhalothrin 15% w/w of 100% purity of Table 7 corresponds to methoxyfenozide 21.32g of 98.5% purity, emamectin benzoate 1.16g of 95% purity and lambda-cyhalothrin 1.57g of 96% purity, of Table 8.

Table 8: Quantities of active ingredients and raw material charged

S. No.	Components	Amount (g)
1	Methoxyfenozide Technical (Basis of 98.5%)	21.32
2	Emamectin Benzoate Technical (Basis of 95%)	1.16
3	Lambda-cyhalothrin Technical (Basis of 96%)	1.57

4	Propylene glycol	5.00
5	Graft copolymer	5.00
6	Non-ionic ethoxylate	3.00
7	Dimethyl Polysiloxane emulsion	0.10
8	20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one	0.10
9	Xanthan gum	0.10
10	Demineralised water	62.65

Example 4: Process of preparing synergistic insecticidal composition comprising methoxyfenozide, emamectin benzoate and lambda-cyhalothrin in suspension concentrate (SC) form

All the components were weighed as per table 8. The graft copolymer (5g) and non-ionic ethoxylate (3g) were diluted in demineralised water and solubilized by high shear mixing. Then propylene glycol (5g), methoxyfenozide (21.32g), emamectin benzoate (1.16g), lambda-cyhalothrin (1.57g), dimethyl polysiloxane emulsion (0.10g), 20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one (0.10g) were added and mixed to obtain a homogeneous mass. The homogeneous mass was grinded in bead mill. The grinding was carried out until a mean particle size of 3-5(D-90) microns was obtained. After grinding, 2% water solution of xanthan gum was added under low stirring to obtain the title insecticidal composition.

Evaluation of bio-efficacy of the synergistic insecticidal composition

Multi-location trials were conducted to evaluate the effect of different insecticidal compositions of present invention (T1-T12) and reference products (T13 – T27) against borer complex and sucking pests of cotton.

Table 9 provides treatment details of various insecticidal compositions. T1-T12 represent synergistic insecticidal composition of the present invention and T13-T27 represent: reference products, such as, solo formulations of methoxyfenozide, emamectin benzoate, pymetrozine, flubendiamide, deltamethrin, lambda-cyhalothrin; and combination products such as methoxyfenozide + emamectin benzoate, methoxyfenozide + pymetrozine, pymetrozine + emamectin benzoate, emamectin benzoate + flubendamide, methoxyfenozide + flubendamide, methoxyfenozide + deltamethrin, emamectin benzoate + deltamethrin, methoxyfenozide + lambda-cyhalothrin and emamectin benzoate + lambda-cyhalothrin.

Table 9: Treatment details for evaluation of bio-efficacy of the synergistic insecticidal composition

Treatments (T)	Details	Dose Formulation g or ml/ha
T1	methoxyfenozide 21%+ emamectin benzoate 1.1% + pymetrozine 15% SC	800
T2	methoxyfenozide 21%+ emamectin benzoate 1.1% + pymetrozine 15% SC	1000
T3	methoxyfenozide 21%+ emamectin benzoate 1.1% + pymetrozine 15% SC	1200
T4	methoxyfenozide 21%+ emamectin benzoate 1.1% + flubendiamide 3.5% SC	800
T5	methoxyfenozide 21%+ emamectin benzoate 1.1% + flubendiamide 3.5% SC	1000
T6	methoxyfenozide 21%+ emamectin benzoate 1.1%	1200

	+ flubendiamide 3.5% SC	
T7	methoxyfenozide 21%+ emamectin benzoate 1.1% + deltamethrin 1.25% SC	800
T8	methoxyfenozide 21%+ emamectin benzoate 1.1% + deltamethrin 1.25% SC	1000
T9	methoxyfenozide 21%+ emamectin benzoate 1.1% + deltamethrin 1.25% SC	1200
T10	methoxyfenozide 21%+ emamectin benzoate 1.1% + lambda-cyhalothrin 1.5% SC	800
T11	methoxyfenozide 21%+ emamectin benzoate 1.1% + lambda-cyhalothrin 1.5% SC	1000
T12	methoxyfenozide 21%+ emamectin benzoate 1.1% + lambda-cyhalothrin 1.5% SC	1200
T13	methoxyfenozide 24% SC	625
T14	emamectin benzoate 5% SG	220
T15	flubendiamide 39.35% m/m SC	125
T16	pymetrozine 50% WP	300
T17	deltamethrin 1.8% EC	781
T18	lambda-cyhalothrin 5% EC	500
T19	methoxyfenozide + emamectin benzoate	625 + 220
T20	methoxyfenozide + pymetrozine	625 + 300
T21	pymetrozine + emamectin benzoate	300 + 220
T22	emamectin benzoate + flubendamide	220 + 125

T23	methoxyfenozide + flubendamide	625 + 125
T24	methoxyfenozide + deltamethrin	625 + 781
T25	emamectin benzoate + deltamethrin	220 + 781
T26	methoxyfenozide + lambda-cyhalothrin	625 + 500
T27	emamectin benzoate + lambda-cyhalothrin	220 + 500

Details of the experiment

The experiment was laid out in Randomized Block Design (RBD) with three replications. The plot size was 100 sq.m. All the recommended agronomic practices were followed throughout the cropping period. The various insecticidal compositions as per Table 9 were sprayed on cotton crop to evaluate the control of borers complex (*Helicoverpa armigera*, Pink Bollworm and *Spodoptera litura*) and sucking Pests (Aphids, Jassids and Whitefly). Hollow cone nozzle was used for spraying. The spray volume used was 500 liters per hectare. Based on various doses, weighed quantity of test products were dissolved in 5 liters of water/treatment and sprayed uniformly twice at an interval of 10 days. Single observation was taken at 10 days after 2nd spray and mean of observations from different locations is presented in Table 10.

For borers complex, 10 plants in each treatment were randomly tagged and total no. of damaged balls/10 plant were recorded before the spray and 10 Days after 2nd spray.

For sucking pests, 10 plants in each treatment were randomly tagged and total number of sucking pest/ per 3 leaves/ 10 plant were recorded before the spray and 10 Days after 2nd spray.

Table 10: The bio-efficacy effect of different treatments on cotton

Treatment	**Borers complex**	**% reducti**	**Sucking pest complex**	**% reducti**
	10 DAS after 2nd		**10 DAS after 2nd**	

	spray*	on over control	spray**	on over control
T1	1.20 (1.30)	87.10	0.97 (1.21)	92.13
T2	0.90 (1.18)	90.32	0.73 (1.11)	94.08
T3	0.70 (1.10)	92.47	0.53 (1.01)	95.70
T4	0.80 (1.14)	91.40	3.53 (2.01)	71.37
T5	0.60 (1.05)	93.55	3.37 (1.97)	72.67
T6	0.30 (0.89)	96.77	3.07 (1.89)	75.10
T7	1.40 (1.38)	84.95	1.30 (1.34)	89.46
T8	1.30 (1.34)	86.02	1.03 (1.24)	91.65
T9	1.10 (1.26)	88.17	0.83 (1.15)	93.27
T10	1.70 (1.48)	81.72	1.53 (1.42)	87.59
T11	1.50	83.87	1.40	88.65

	(1.41)		(1.38)	
T12	1.20 (1.30)	87.10	1.37 (1.37)	88.89
T13	5.30 (2.41)	43.01	8.57 (3.01)	30.49
T14	5.60 (2.47)	39.78	8.21 (2.95)	33.41
T15	6.10 (2.57)	34.41	7.15 (2.77)	42.01
T16	7.20 (2.77)	22.58	6.19 (2.59)	49.80
T17	7.90 (2.90)	15.05	6.67 (2.68)	45.90
T18	8.30 (2.97)	10.75	6.80 (2.70)	44.85
T19	3.30 (1.95)	64.51	6.13 (2.57)	50.28
T20	4.90 (2.32)	47.31	4.37 (2.21)	64.56
T21	4.50 (2.24)	51.61	3.83 (2.08)	68.94
T22	2.10 (1.61)	77.42	6.13 (2.57)	50.28

T23	2.00 (1.58)	78.49	6.80 (2.70)	44.85
T24	3.20 (1.92)	65.59	5.43 (2.44)	55.96
T25	2.90 (1.84)	68.82	5.97 (2.54)	51.58
T26	2.80 (1.82)	69.89	6.67 (2.68)	45.90
T27	3.00 (1.87)	67.74	6.10 (2.57)	50.53
Control	9.30 (3.13)	--	12.33 (3.58)	--
SE(m)	**0.200**	-	**0.228**	-
C.D.	**0.567**	-	**0.649**	-

Figure in parenthesis represents square root transformed value

*(Mean No./per 10 plants) **(Mean No./ per 3 leaves/10 plants)

Synergistic effect of the composition of the present invention

A synergistic effect exists whenever the action of an active ingredient combination is greater than the sum of the actions of the individual components. Synergism was calculated by using Colby's method, *Weeds, vol 15 No. 1(Jan 1967), pp 20-2.*

The synergistic action expected for a given combination of three active components can be calculated as follows:

$$E = X+Y+Z - \{XY+YZ+YZ\} + \frac{(XYZ)}{100} \qquad \frac{}{10000}$$

Where E represents expected percentage of insecticidal control for the combination of the three insecticides at defined doses (for example equal to x, y and z respectively), X is the percentage of insecticidal control observed by the compound (I) at a defined dose (equal to x), Y is the percentage of insecticidal control observed by the compound (II) at a defined dose (equal to y), Z is the percentage of insecticidal control observed by the compound (III) at a defined dose (equal to z). When the percentage of insecticidal control observed for the combination is greater than the expected percentage, there is a synergistic effect.

In the same experiment, to evaluate synergistic impact, mean control of both borers (% reduction of ball damage against control) and sucking pests (% insect control) were taken for insecticidal treatments. Table 11 summarizes the synergistic impact of the composition of the present invention.

Table 11: Synergistic impact of the composition of the present invention

S. No.	Treatment	Dose g a.i./ha	Mean control % (observed)	Expected Control	Colby Ratio
1	Methoxyfenozide 21%+ Emamectin benzoate 1.1% + Pymetrozine 15% SC	210+11+150	92.20	74.41	1.24
2	Methoxyfenozide 21%+ Emamectin benzoate 1.1% + Flubendiamide 3.5% SC	210+11+35	83.11	75.22	1.10

3	Methoxyfenozide 21%+ Emamectin benzoate 1.1% + Deltamethrin 1.25% SC	210+11+12.5	88.84	72.12	1.23
4	Methoxyfenozide 21%+ Emamectin benzoate 1.1% + Lambda-cyhalothrin 1.5% SC	210+11+25	86.26	71.05	1.21
5	Methoxyfenozide + Emamectin-Benzoate (Tank mix)	210+11	57.40	53.71	1.07
6	Methoxyfenozide + Pymetrozine (Tank mix)	210+ 150	55.94	65.11	0.86
7	Pymetrozine + Emamectin-Benzoate (Tank mix)	150+11	60.28	66.57	0.91
8	Emamectin-Benzoate + Flubendamide (Tank mix)	11+60	63.85	61.38	1.04
9	Methoxyfenozide + Flubendamide (Tank mix)	210+60	61.67	59.69	1.03
10	Methoxyfenozide + Deltamethrin (Tank mix)	210+12.5	60.78	62.40	0.97
11	Emamectin-Benzoate + Deltamethrin (Tank mix)	11+12.5	60.20	63.97	0.94
12	Methoxyfenozide + Lambda-cyhalothrin (Tank mix)	210+25	57.90	61.67	0.94
13	Emamectin-Benzoate + Lambda-cyhalothrin (Tank mix)	11+25	59.14	63.28	0.93
14	Methoxyfenozide 24% SC	210	36.75	--	--
15	Emamectin-Benzoate 5% SG	11	36.60	--	--

16	Flubendiamide 39.35% m/m SC	60	38.21	--	--
17	Pymetrozine 50% WP	150	36.19	--	--
18	Deltamethrin 1.8% EC	12.5	30.48	--	--
19	Lambda-cyhalothrin 5% EC	25	27.80	--	--

It is evident from table 11 that the composition of the present invention is synergistic (S.No.1 - S.No.4) as the observed value of mean percentage control of pests is greater than the expected mean percentage control of pests. It can be further observed that for the treatment corresponding to S.No.2, the dose of flubendiamide is lower than the tank mix and solo formulations, still the percentage control of pests is higher for the treatment corresponding to S.No.2.

Comparative Example

The experiment was laid out in Randomized Block Design (RBD) with three replications. The plot size was 25 sq. m. All the recommended agronomic practices were followed throughout the cropping period. The various insecticidal compositions as per Table 12 were sprayed on cabbage crop to evaluate the diamond back moth (larval population). The spray volume used was 500 liters per hectare. Based on various doses, weighed quantity of test products were dissolved in 1.25 liter of water/treatment/replication and sprayed uniformly using hand held pressure sprayer. Observations were taken at DBS (day before spray), 3, 7 and 14 days after spray (DAS).

Table 12 provides comparative data of the compositions of the present invention and the compositions of the prior art. It is evident that the composition of the present invention provides better control of diamond back moth (larval population) as compared to the composition of the prior art such as, methoxyfenozide 17.5%+ emamectin benzoate 1% + bifenthrin 7.5%SC, methoxyfenozide 17.5%+ emamectin benzoate 1% + profenofos 30%EC, methoxyfenozide 17.5%+ emamectin benzoate 1%+ thiamethoxam 12.5%SC.

Table 12:

Sr. No.	Treatment	Dose (g/ml/ha)	Diamond Back Moth (larval Population)				
			DBS	3 DAS	7DAS	14 DAS	% larval control after 14DAS
1	Methoxyfenozide 21% + Emamectin benzoate 1.1% + Pymetrozine 15% SC	1000	3.70 (2.05)	2.30 (1.67)	1.50 (1.41)	1.00 (1.22)	81.13
2	Methoxyfenozide 21% + Emamectin benzoate 1.1% + Flubendiamide 3.5% SC	1000	3.80 (2.07)	1.00 (1.22)	0.20 (0.84)	0.10 (0.77)	98.11
3	Methoxyfenozide 21% + Emamectin benzoate 1.1% + Deltamethrin 1.25% SC	1000	3.90 (2.10)	1.20 (1.30)	0.50 (1.00)	0.40 (0.95)	92.45
4	Methoxyfenozide 21% + Emamectin benzoate 1.1% + Lambda-cyhalothrin 1.5% SC	1000	4.10 (2.14)	1.40 (1.38)	0.40 (0.95)	0.30 (0.89)	94.34

5	Methoxyfenozide 17.5% + Emamectin benzoate 1% +Bifenthrin 7.5%SC	1000	3.90 (2.10)	2.50 (1.73)	1.80 (1.52)	1.60 (1.45)	69.81
6	Methoxyfenozide 17.5%+ Emamectin benzoate 1%+ Profenofos 30%EC	1000	4.30 (2.19)	2.30 (1.67)	1.80 (1.52)	1.50 (1.41)	71.70
7	Methoxyfenozide 17.5% + Emamectin benzoate 1% + Thiamethoxam 12.5%SC	1000	4.10 (2.14)	2.60 (1.76)	2.10 (1.61)	1.70 (1.48)	67.92
8	Control	--	3.90 (2.10)	4.40 (2.21)	4.90 (2.32)	5.30 (2.41)	
	SE(m)	-	**0.015**	**0.082**	**0.117**	**0.129**	
	C.D.	-	**0.045**	**0.253**	**0.357**	**0.395**	

DBS: Days before spray

DAS: Days after spray

Phytotoxicity Observations

For phytotoxicity evaluation on cotton, following observations were made by observing temporary or long lasting damage to the leaves if any viz., leaf injury on tips and leaf surface, wilting, vein clearing, necrosis, epinasty and hyponasty after 14 DAS of the synergistic insecticidal composition of the present invention (T1-T12). The treatment details were per Table 9. Crop injury was observed on visual rating from 1-10 scale as given in Table 13. Table 14 provides phytotoxic effect of the synergistic composition of the present invention on cotton.

Table 13:

Rating	Crop Injury (%)	Verbal Description
0	-	No symptoms
1	1-10	Very slight discoloration
2	11-20	More severe, but not lasting
3	21-30	Moderate and more lasting
4	31-40	Medium and lasting
5	41-50	Moderately heavy
6	51-60	Heavy
7	61-70	Very Heavy
8	71-80	Nearly destroyed
9	81-90	Destroyed
10	91-100	Completely destroyed

Table 14. Phytotoxic effect of synergistic composition of the present invention on cotton

Treatments	Phytotoxicity rating					
	Leaf tip injury	Wilting	Vein Clearing	Necrosis	Epinasty	Hyponasty
1	0	0	0	0	0	0
2	0	0	0	0	0	0
3	0	0	0	0	0	0
4	0	0	0	0	0	0

5	0	0	0	0	0	0
6	0	0	0	0	0	0
7	0	0	0	0	0	0
8	0	0	0	0	0	0
9	0	0	0	0	0	0
10	0	0	0	0	0	0
11	0	0	0	0	0	0
12	0	0	0	0	0	0

The synergistic insecticidal composition of the present invention gave good control of insects as compared to the reference products. Further, the use of the synergistic insecticidal composition resulted in better crop condition, i.e. fresh green leaves and did not produce any phytotoxic symptoms on the plants.

From the foregoing it will be observed that numerous modifications and variations can be effectuated without departing from the true spirit and scope of the novel concepts of the present invention. It is to be understood that no limitations with respect to the specific embodiments illustrated is intended or should be inferred. It should be understood that all such modifications and improvements have been deleted herein for the sake of conciseness and readability but are properly within the scope of the following claims.

Claims:

1. A synergistic insecticidal composition comprising:

   a) 15 to 25%w/w of methoxyfenozide;

   b) 0.1 to 3%w/w of emamectin benzoate;

   c) 0.5 to 20%w/w of one of pymetrozine, flubendiamide, deltamethrin, and lambda-cyhalothrin; and

   d) at least one excipient.

2. The synergistic insecticidal composition as claimed in claim 1, comprising 21% w/w of methoxyfenozide, 1.1%w/w of emamectin benzoate and 15% w/w of pymetrozine.

3. The synergistic insecticidal composition as claimed in claim 1, comprising 21% w/w of methoxyfenozide, 1.1%w/w of emamectin benzoate and 3.5% w/w of flubendiamide.

4. The synergistic insecticidal composition as claimed in claim 1, comprising 21% w/w of methoxyfenozide, 1.1%w/w of emamectin benzoate and 1.25%w/w of deltamethrin.

5. The synergistic insecticidal composition as claimed in claim 1, comprising 21% w/w of methoxyfenozide, 1.1%w/w of emamectin benzoate and 1.5%w/w of lambda-cyhalothrin.

6. The synergistic insecticidal composition as claimed in claim 1, wherein the composition is formulated as Capsule suspension (CS), Dispersible concentrate (DC), Dustable powder (DP), Powder for dry seed treatment (DS), Emulsifiable concentrate (EC), Emulsifiable granule (EG), Emulsion water-in-oil (EO), Emulsifiable powder (EP), Emulsion for seed treatment (ES), Emulsion oil-in-water (EW), Flowable concentrate for seed treatment (FS), Granules (GR), Micro-emulsion (ME), Oil-dispersion (OD), Oil miscible flowable concentrate (OF), Oil miscible liquid (OL), Oil dispersible powder (OP), Suspension concentrate (SC), Suspension concentrate for direct

application (SD), Suspo-emulsion (SE), Water soluble granule (SG), Soluble concentrate (SL), Spreading oil (SO), Water soluble powder (SP), Water soluble tablet (ST), Ultra-low volume (ULV) suspension, Tablet (TB), Ultra-low volume (ULV) liquid, Water dispersible granules (WG), Wettable powder (WP), Water dispersible powder for slurry seed treatment (WS), Water dispersible tablet (WT), a mixed formulation of CS and SC (ZC) or A mixed formulation of CS and SE (ZE), a mixed formulation of CS and EW (ZW).

7. The synergistic insecticidal composition as claimed in claim 6, wherein the composition is formulated as suspension concentrate.

8. The synergistic insecticidal composition, as claimed in claim 1, wherein the excipient is selected from the group comprising dispersing agent, wetting agent, anti-freezing agent, defoamer, biocide and thickener.

9. The synergistic insecticidal composition as claimed in claim 8, wherein the dispersing agent is selected from the group comprising amine salt of phosphate tristyryl phenol ethoxylated, acrylic copolymer, graft copolymer and combinations thereof, and present in an amount in the range from 2 to 10% w/w.

10. The synergistic insecticidal composition as claimed in claim 8, wherein the wetting agent is selected from the group comprising ethoxylated polyarylphenol phosphate ester, dioctyl sulphosuccinate, non-ionic ethoxylate and combinations thereof, and present in an amount in the range from 1 to 5% w/w.

11. The synergistic insecticidal composition as claimed in claim 8, wherein the anti-freezing agent is selected from the group comprising propylene glycol, diethylene glycol, monoethylene glycol and combinations thereof, and present in an amount in the range from 2 to 10% w/w.

12. The synergistic insecticidal composition as claimed in claim 8, wherein the defoamer is dimethyl polysiloxane emulsion and present in an amount in the range from 0.01 to 0.5% w/w.

13. The synergistic insecticidal composition as claimed in claim 8, wherein the biocide is selected from the group consisting of 20% aqueous dipropylene glycol solution of 1,2-benzisothiazolin-3-one, formaldehyde and combinations thereof and present in an amount in the range from 0.01 to 0.50% w/w.

14. The synergistic insecticidal composition as claimed in claim 8, wherein the thickener is xanthan gum and present in an amount in the range from 0.01 to 0.50% w/w.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER
A01N53/00,A01N47/40 Version=2020.01

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 practicable, search terms used)

TotalPatent One, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	IN201621027690 (GSP CROP SCIENCE PVT. LTD.) 16 FEBRUARY 2018 (16-02-2018) Claims 1-7, Table 2, pages 16-19,49	1-14
A	CN104304331A (LI JIE) 28 JANUARY 2015 (28-01-2015) abstract, claims 1-4	1-14

☐ Further documents are listed in the continuation of Box C. ☐ 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
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"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
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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Authorized officer Preeti Bansal Telephone No. +91-1125300200