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(54) Title: SYNERGISTIC GRANULAR INSECTICIDAL COMPOSITION

(57) Abstract: The present invention relates to a synergistic granular insecticidal composition and manufacturing method thereof. More specifically, it relates to a synergistic granular insecticidal composition comprising A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives; B) Fipronil or its agrochemically acceptable salts, esters and derivatives and C) Emamectin or its agrochemically acceptable salts, esters and derivatives. The present invention also relates to a process for preparation of such synergistic granular insecticidal composition for foliar spray treatment of plants and soil application treatment for synergistic and efficacious control of insect pests and improved plant yield.

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SYNERGISTIC GRANULAR INSECTICIDAL COMPOSITION

FIELD OF THE INVENTION

The present invention relates to a synergistic granular insecticidal composition and manufacturing method thereof. More specifically, it relates to a synergistic granular insecticidal composition comprising A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives; B) Fipronil or its agrochemically acceptable salts, esters and derivatives and C) Emamectin or its agrochemically acceptable salts, esters and derivatives. The present invention also relates to a process for preparation of such synergistic granular insecticidal composition for foliar spray treatment of plants and soil application treatment for synergistic and efficacious control of insect pests and improved plant yield.

BACKGROUND OF THE INVENTION

Insect pests are one of the worst enemies of crops. They cause severe damages to the crops resulting in reduced crop productivity. Controlling crop pest population has been a major issue and various traditional and advanced means are being used to minimize the damage caused by insect pests. Continuous use of pesticides and insecticides in uncontrolled and unscientific manner over the years has resulted in development of resistance in the insect pests and this resistance continues to broaden in spectrum against the number of insecticides/pesticides. Continuous high intensity use of insecticides and pesticides has given rise to other critical issues like presence of high quantity of insecticide residues in agricultural products, increasing environmental pollution and damage to ecological balance and deteriorating health of consumers. With the onset of resistance to certain insect pests, there is a need in the art for a combination of actives that decrease the chances of resistance and improves the spectrum of disease and pest control.

In a recent agriculture environment in which number of incoming populations is reduced and population is aging, saving labor for cultivation and management of crop becomes a very urgent issue. To control insect pests, it is necessary to spray and use a insecticide effective for target insect pests at appropriate times throughout the cultivation period. An insect pest control system is typically formed by spraying and using insecticides several times. That is, in case where the insecticide has imperfect time- release function, using the insecticide at a time may cause risks of

inflicting chemical harms, and therefore, the ideal labor-saving pest control method was not achieved practically.

As such, it was required to completely or minimally reduce the leakage of insecticide active ingredients into the environment during the release restraining period to establish a labor-saving cultivation method, composition.

Amongst other available formulations, composition, granular insecticidal composition is a highly safe formulation form, but a formulation in which the insecticidal active ingredient is released in a short period of time causes problems such as a shortened duration of efficacy and phytotoxicity. In order to solve these problems, it is necessary to control the elution of the insecticidal active ingredients from the granular insecticide composition in water, and various attempts have been made for this purpose. To realize this, granular insecticide compositions are necessary which have a function to restrain the release or discharge of the various types of insecticides into the environment until reaching necessary times, to immediately initiate the release of an insecticidal active ingredient at an appropriate timing, and to continue the release of the insecticidal active ingredient during a desired period even at low doses of the actives in the composition.

Thus, it is essential to reduce the amount of active insecticidal ingredients released into the environment while still ensuring effective pest control. Although many granular insect pest control combinations have been studied, a high synergistic action has not always been found. There is a need for improved combinations. Single and binary active compositions used over long period of time have resulted in resistance. With the onset of resistance to certain insect pests, there is a need in the art for a synergetic granular insecticidal compositions comprising combination of actives that not only decrease the chances of resistance development, and at the same time broadens the spectrum of disease and insect pest control.

An effective insect, pest control can be achieved by combining insecticidal active ingredients in appropriate weight percentage range for obtaining stable and effective formulation. In addition to this, stability of active ingredients and user-friendliness are also important parameters to be taken into account while choosing the formulation type, and surfactants or adjuvants.

Combining other actives with anthranilic diamide insecticides causes compatibility issues, making it difficult to develop a stable composition comprising anthranilic diamide insecticides, which provides efficacious and synergistic results against insect pests is a tedious task. Therefore, to solve the aforementioned conventional problems, the present inventors have arrived at a granular insecticidal composition comprising anthranilic diamide insecticides with other insecticides having low doses, which may be produced with low costs, causes less environmental pollution by virtue of low toxicity and biodegradability, achieve highly sophisticated release control and also provide improved plant/crop yield, growth.

Further, damage to plants from pests including insects is a major concern for agriculturist. There are various plant diseases, which reduce the water and nutrient uptake in plants and decrease the overall yield of the crops. Treating plants with such insecticides and micronutrients combination helps reduce the damage from insect pests. Another advantage of treating the plants with the said combination is the improvement in plant growth, increased yield and overall plant health. For the reasons mentioned above there is a need to provide further a granular insecticidal composition with combination of three insecticides as actives at low doses having synergistic insect pest control properties along with micronutrients. This object is achieved according to the invention by providing the present stable synergistic granular insecticidal composition.

There are various prior arts which disclose compositions comprising combination of insecticide actives with anthranilic diamide insecticides with other insecticides. Some of such prior arts are listed below:

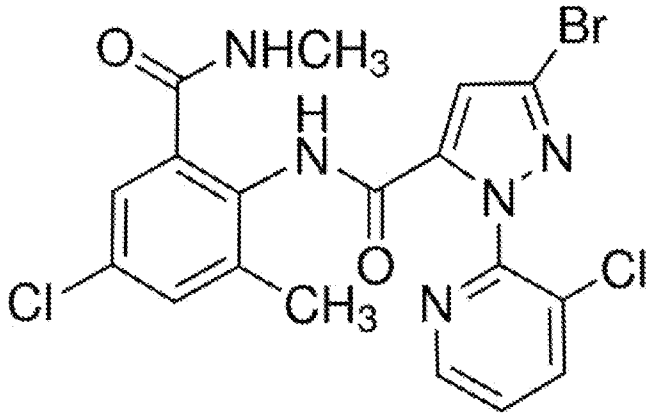
CN103651419 discloses a chlorantraniliprole-Emamectin benzoate, suspending agent and a preparation method thereof. The effective components of the composition comprise 1-20% of chlorantraniliprole, 1-10% of Emamectin benzoate, 3-6% of a dispersant, 0.5-3% of a lubricant, 0.1-1% of a stabilizer, 0.05-0.2% of a defoamer, 0.2-5% of a suspending agent, 3-5% of an anti-freezing agent and the remaining water.

IN202217040171 discloses an insecticidal composition that comprises a combination of (i) an anthranilamide compound of formula (I); and (ii) at least one insecticidal compound, wherein the weight ratio of the anthranilamide compound of formula (I) to the insecticidal compound is from about 1:100 to 100:1.

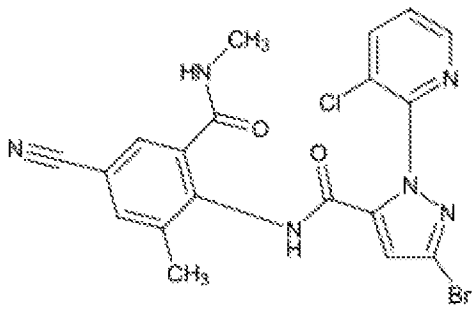
IN202021030669 discloses a synergistic mixture for plant treatment comprising of an insecticide from the diamide group of insecticide; one or more plant health additives; and one more insecticides.

Diamide insecticides such as anthranilic diamides are a new class of insecticides that provide good control through action on a novel target, the ryanodine receptor. Anthranilic diamides potentially activate this receptor, releasing stored calcium from the sarcoendoplasmic reticulum causing impaired regulation of muscle contraction and thus the cell death. Anthranilic diamides are an important commercial synthetic class of insecticides that bind to the ryanodine receptor with selective potency against insect versus mammalian forms of the receptor. Some of such anthranilic diamide insecticides are cyantraniliprole, tetraniliprole, cyclaniliprole, tetrachlorantraniliprole and chlorantraniliprole. The first commercialized diamide, Chlorantraniliprole, has exceptional activity against lepidopteran pests. The second anthranilamide product, cyantraniliprole, has excellent cross-spectrum activity against a range of insect orders, including both lepidopteran and hemipteran pests.

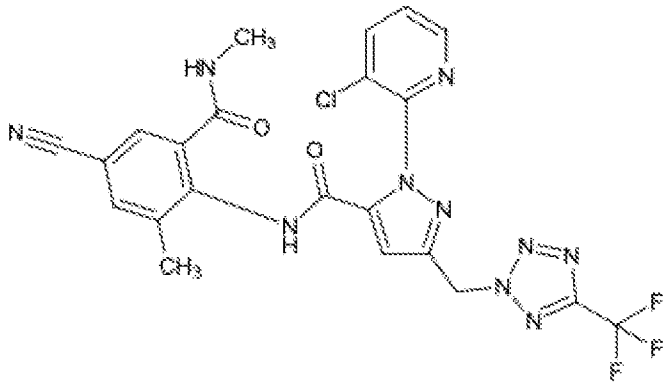
Chlorantraniliprole also known as 5-bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-2-(3-chloropyridin-2-yl)pyrazole-3-carboxamide, is a anthranilic-diamide insecticide. It is broad spectrum insecticide for the effective control of Stem borer& Leaf folder for rice, Diamond Back Moth for cabbage, American Boll warm, spotted bollworm & Tobacco caterpillar for Cotton, termite, early shoot borer & Top borer for Sugarcane, Fruit borer for Tomato & Chilli, Green semiloopers &stem fly Girdle Beetle for soyabean, Fruit and shoot borer for Brinjal, Gram pod borer & pod fly for pigeon pea, Pod borer for Bengal gram & Black gram, Fruit borer & caterpillars for Bitter gourd, Fruit borer for Okra, Spotted stem borer, pink stem borer for maize, Tobacco Caterpillar for Ground nut. Chemical structure of Chlorantraniliprole is provided below:



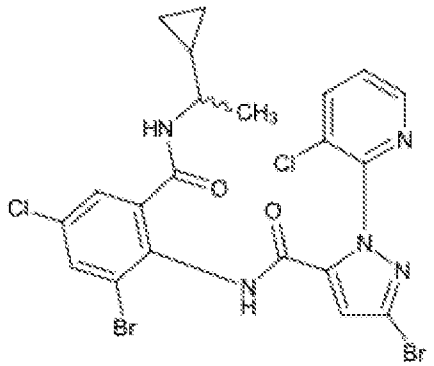
Cyantraniliprole: chemical name: 3-bromo-1- (3-chloro-2-pyridinyl) -N- { 4-cyano-2-methyl-6- [(methylamino) carbonyl] phenyl } -1H-pyrazole-5-carboxamide. It is a high-efficiency and safe dimethylformamide pesticide. Cyantraniliprole shows action mechanism of the pesticide is to activate a ryanodine receptor (ryanodine receptor), so that intracellular calcium ions are released unlimitedly, thereby causing relaxation paralysis, activity pause and paralysis of insect muscles until the insect muscles die completely, and the pesticide can effectively prevent and treat lepidoptera, homoptera, hemiptera, coleopteran and thysanoptera pests. Cyantraniliprole has the structure provided below:



Tetraniloprole (Tetratolanilide) is a diamide insecticide belonging to anthranilamide insecticides, has an action mechanism that acts by activating ryanodine receptors in calcium release channels, causes the loss of control and paralysis of insect muscles, and can be used for preventing and treating lepidoptera, coleopteran and dipteran pests. Tetraniloprole has the structure provided below:

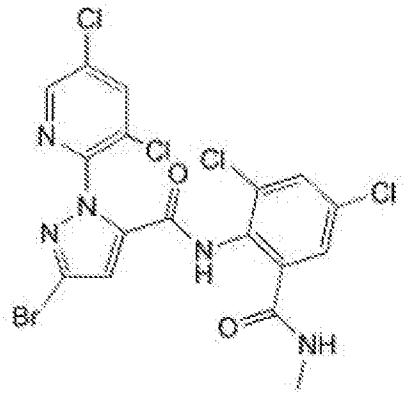


Cyclaniliprole is cyclic bromantraniliprole, having the chemical name: 3-bromo-N- [2-bromo-4-chloro-6- [[(1-cyclopropylethyl) amine] carbonyl] phenyl] -1- (3-chloro-2-pyridine) -1H-pyrazole-5-carboxamide. Cyclaniliprole has systemic activity and broad-spectrum insecticidal activity, and has good control effect on pests such as diamondback moth, prodenia litura, whitefly, aphid, thrips, liriomyza and the like. Cyclaniliprole has the structure provided below:

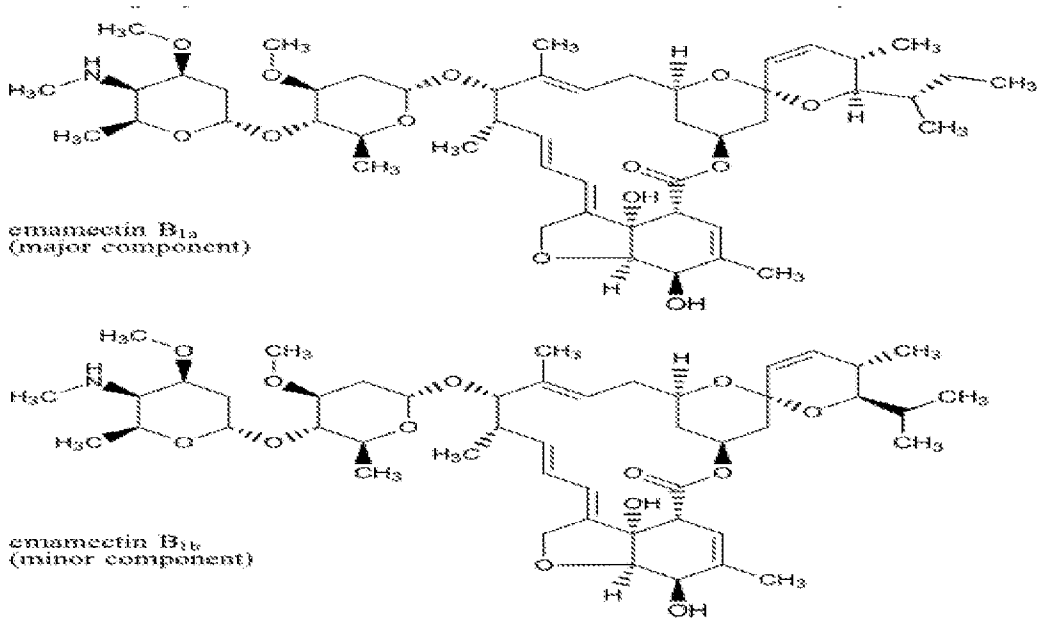


Tetrachlorantraniliprole belongs to a ryanodine insecticide, and is used for continuously releasing calcium ions stored in cells into sarcoplasm by combining with ryanodine receptors in pests to open calcium ion channels, and the calcium ions are combined with matrix proteins in the sarcoplasm to cause the muscle to continuously contract. Insect symptoms are manifested as convulsions, food refusal, and ultimately death. Tetrachlorantraniliprole is a low-toxicity, broad-spectrum pesticide and has good activity on lepidoptera pests. The control objects comprise rice leaf rollers, chilo suppressalis, diamond back moths, asparagus caterpillars, corn borers,

sugarcane borers, diamond back moths, carposina niponensis walsingham and the like. Tetrachlorantraniliprole has the structure provided below:



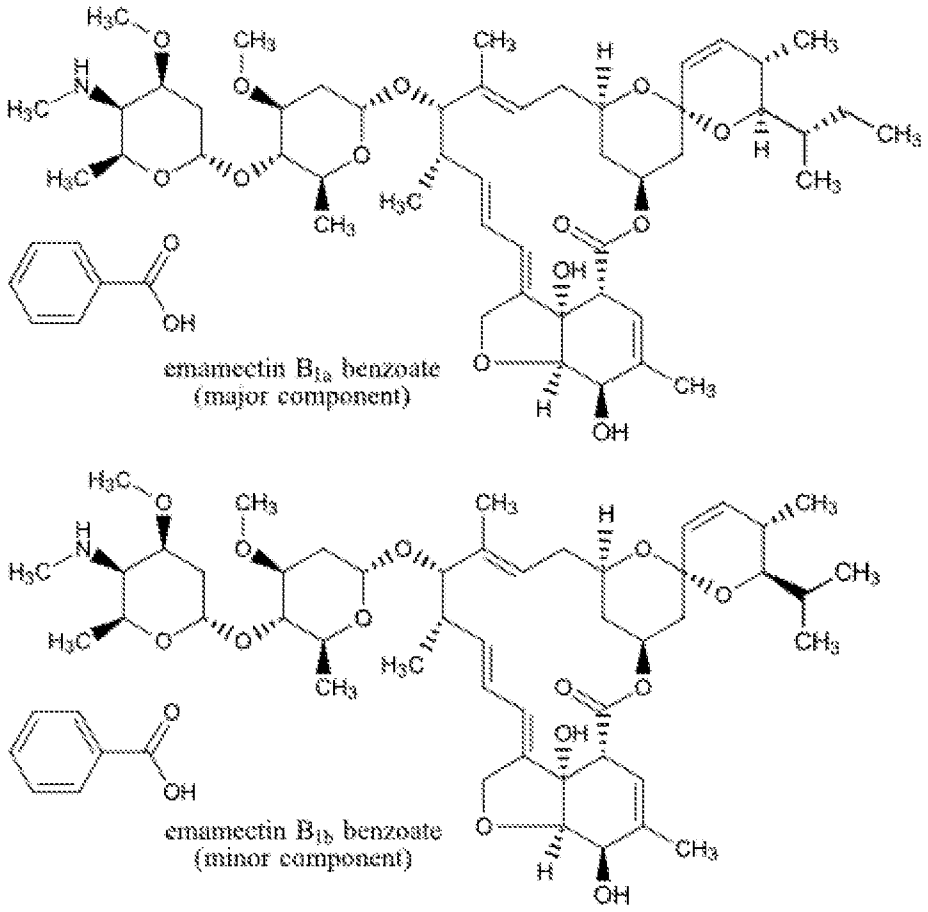
Emamectin is a macrocyclic lactone insecticide with low toxicity to non-target organisms and the environment, and is considered an important component in pest-management programmes for controlling field crop pests. Emamectin belongs to the avermectin family, which exhibit toxicity for nematodes, arthropods, and several other pests. Emamectin is derived from avermectin B1, also known as abamectin, a mixture of the natural avermectin B1a and B1b. Emamectin, belongs to the avermectin family of compounds all of which exhibit toxicity for nematodes, arthropods, and several other pests. The benzoate salt of emamectin in particular has found widespread use as an insecticide and is approved by the EPA for use in prevention of emerald ash borer in ash trees. Emamectin works as a chloride channel activator by binding gamma aminobutyric acid (GABA) receptor and glutamate-gated chloride channels disrupting nerve signals within arthropods. Emamectin is widely used in controlling lepidopterous pests (order of insects that as larvae are caterpillars and as adults have four broad wings including butterflies, moths, and skippers) in agricultural products. Chemical structure of Emamectin is provided below:



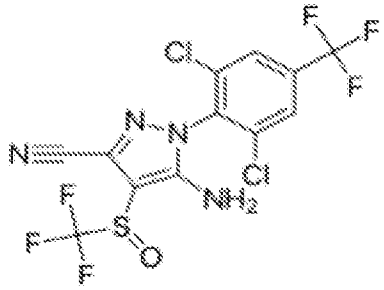
Emamectin benzoate is the 4'-deoxy-4'-epi-methyl-amino benzoate salt of avermectin B1 (abamectin), which is similar structurally to natural fermentation products of Streptomyces avermitilis. Emamectin benzoate is being developed as a newer broad-spectrum insecticide for vegetables and has a very low application rate. The mechanism of action involves stimulation of high-affinity GABA receptors and a consequent increase in membrane chloride ion permeability.

Emamectin benzoate with the chemical name of 4 '-methylamino-4' -deoxyabamectin B1 benzoate is a novel high-efficiency semisynthetic antibiotic type insecticidal and acaricidal pesticide, and the action mechanism of the emamectin benzoate is to interfere the nerve physiological activity of insects, stimulate and release gamma-aminobutyric acid and inhibit the

conduction of nerve impulse of the insects. Emamectin benzoate has the structure shown below:



Fipronil belongs to phenylpyrazole class of insecticide and acaricide with chemical name of 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile. Fipronil is a broad-spectrum insecticide that belongs to the phenylpyrazole chemical family. Fipronil is used in a wide variety of pesticide products, including granular products for grass, gel baits, spot-on pet care products, liquid termite control products, and products for agriculture. Fipronil disrupts the insect central nervous system by blocking the ligand-gated ion channel of the GABAA receptor and glutamate-gated chloride (GluCl) channels. This causes hyperexcitation of contaminated insects' nerves and muscles. Fipronil has the structure shown below:



Thus, the present invention combines the above mentioned three insecticides in a granular insecticidal composition, which releases the insecticides at slow rate to achieve effective and synergetic control of insect pests.

Further, micronutrients reduce the need for fertilizers and increase plant growth, resistance to water and abiotic stresses. In small concentrations, these substances are efficient, favoring the good performance of the plant's vital processes, and allowing high yields and good quality products. In addition, micronutrients applied to plants, crops enhance nutrition efficiency, abiotic stress tolerance and/or plant quality traits. Various micronutrients are being used in agrochemical compositions, however, the judicious use of micronutrients with insecticidal compositions comprising anthranilic diamide insecticides, Fipronil and Emamectin/Emamectin Benzoate leads to improved plant growth and yield apart from favourable, effective and synergistic control of insect pests.

The present invention thus further combines micronutrients to the granular insecticidal composition comprising anthranilic diamide insecticides with Fipronil and Emamectin or the agrochemically acceptable salts, esters and derivatives of these actives. The present invention overcomes the drawbacks of the prior arts by providing synergistic granular insecticidal compositions comprising combinations of above mentioned active ingredients along with agrochemically acceptable excipients. The granular insecticidal composition of the present invention is stable as well as provide desired bio-efficacy, synergy and prolonged effect. The present invention further provides a novel method of preparing granular insecticidal composition comprising above mentioned active ingredients, which composition is stable as well as provide desired bio-efficacy, synergy.

OBJECTIVES OF THE INVENTION

Accordingly, the main objective of the present invention is to provide a synergistic granular insecticidal composition for insect pest control of plants, crops.

Another objective of the present invention is to provide a synergistic granular insecticidal composition which provides controlled release of the active ingredients and prolonged insect control.

Yet another objective of the present invention is to provide a synergistic granular insecticidal composition that promotes plant health and increase plant, crop yield in the field.

Another objective of the present invention is to provide a stable, synergistic granular insecticidal composition comprising A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives; B) Fipronil or its agrochemically acceptable salts, esters and derivatives and C) Emamectin or its agrochemically acceptable salts, esters and derivatives.

Yet another objective of the present invention is to provide a process for the preparation of a stable, synergistic granular insecticidal composition comprising A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives; B) Fipronil or its agrochemically acceptable salts, esters and derivatives and C) Emamectin or its agrochemically acceptable salts, esters and derivatives.

Further objective of the present invention is to provide a stable, synergistic granular insecticidal composition which is a controlled –release type insecticidal granular formulation that causes less environmental pollution due to low toxicity and biodegradability, achieve a highly sophisticated release control.

It is another objective of the present invention to provide a stable, synergistic granular insecticidal composition which has low cost and is easy to manufacture.

It is another objective of the present invention to provide a synergistic granular insecticidal composition which is a controlled –release type insecticidal granular formulation which is stable at various temperature and pH conditions.

It is yet another objective of the present invention to provide a novel and effective synergistic granular insecticidal composition, with improved stability over the desired shelf life.

It is another objective of the present invention to provide a novel and effective synergistic granular insecticidal composition, which is economically more beneficial.

It is another objective of the present invention to provide a novel and effective synergistic granular insecticidal composition which has both preventive and curative action and is active against all life stages of major insects.

It is another objective of the present invention to provide a novel and effective synergistic granular insecticidal composition that allows adequate sustained-release of an agrochemical active ingredient for effective control of insect pests without resistance.

It is another objective of the present invention to provide a novel and effective synergistic granular insecticidal composition which is environmentally safe, possesses broad spectrum bio-efficacy, is non-phytotoxic.

It is another objective of the present invention to provide a novel and effective synergistic granular insecticidal composition which provides maximum benefit with reduced cost thus providing higher benefit: cost ratio.

It is another objective of the present invention to provide a novel and effective synergistic granular insecticidal composition which avoids degradation of the formulation and allows for gradual release of insecticidal actives to the area of action on the plant and crops.

Some or all these and other objects of the invention can be achieved by way of the invention described hereinafter.

SUMMARY OF THE INVENTION:

In summary, the present invention relates to a synergistic granular insecticidal composition comprising A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives; B) Fipronil or its agrochemically acceptable salts, esters and derivatives and C) Emamectin or its agrochemically acceptable salts, esters and derivatives. The present invention also relates to a process for preparation of such synergistic granular insecticidal

composition for foliar spray treatment of plants and soil application treatment for synergistic and efficacious control of insect pests and improved plant health, yield.

In one embodiment, the present invention provides a controlled release granular insecticidal composition which is stable, easy to handle, environmentally safe and cost effective.

In one embodiment, the present invention provides a synergistic granular insecticidal composition comprising bioactive amounts of:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives;

B) Fipronil or its agrochemically acceptable salts, esters and derivatives and

C) Emamectin or its agrochemically acceptable salts, esters and derivatives.

In another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; and

C) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

C) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition; and

D) agrochemically acceptable excipients.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present as 0.45% by weight of the composition;

B) Emamectin or its agrochemically acceptable salts, esters and derivatives, present as 0.18% by weight of the composition; and

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present as 0.5% by weight of the composition.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) Chlorantraniliprole or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; and

C) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition.

In one another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) Chlorantraniliprole or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; and

C) Emamectin Benzoate, present in the range of 0.01 to 1% by weight of the composition.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) Chlorantraniliprole, present as 0.45% by weight of the composition;

B) Emamectin or its agrochemically acceptable salts, esters and derivatives, present as 0.18% by weight of the composition; and

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present as 0.5% by weight of the composition.

In one another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) Chlorantraniliprole, present as 0.45% by weight of the composition;

B) Emamectin Benzoate, present as 0.18% by weight of the composition; and

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present as 0.5% by weight of the composition.

In yet another preferred embodiment, the present invention provides a synergistic controlled release granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; and

D) one or more agrochemically acceptable excipients.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition wherein the anthranilic diamide insecticide is selected from Chlorantraniliprole, Cyantraniliprole, Tetraniliprole, Cyclaniliprole and Tetrachlorantraniliprole.

Various micronutrients are also used in the composition of present invention including but not limited to Zinc (zinc sulphate heptahydrate $ZnSO_4$7H2O, zinc sulphate mono hydrate $ZnSO_4$.H2O, chelated zinc as Zn-10 EDTA, zinc oxide, Zinc Lactate Gluconate, Zinc Polyflavonoid), Boron (borax-sodium tetraborate, boric acid (H3BO3), di-sodium octa borate tetra hydrate (Na2B8O13.4H2O), di-sodium tetra borate penta hydrate, anhydrous borax,), Manganese (manganese sulphate), Copper (copper sulphate), Iron (ferrous sulphate, chelated iron as Fe-EDTA), Molybdenum (ammonium molybdate), Magnesium (Magnesium sulphate) or Sulphur (elemental sulphur, boronated sulphur) and /or mixtures thereof.

Zinc deficiency in crop plants is the most common micronutrient deficiency; it is particularly common in high-pH soils. Plants that grow in soils that are zinc-deficient are more susceptible to disease. Zinc is required for normal healthy plant, animal, and human growth and reproduction. Crop yields and crop product quality suffer when plant-available zinc is scarce. Zinc is an essential structural constituent or regulatory cofactor of many different enzymes and proteins in many important biochemical pathways in plants. Plant growth suffers when the plant's zinc supply is insufficient. This can cause visible stress symptoms within the plant, which can include stunting (reduced height), interveinal chlorosis (yellowing of the leaves between the veins), bronzing of chlorotic leaves, small and abnormally shaped leaves, and/or stunting and rosetting of leaves (where the leaves form a whorl on shortened stems).

Zinc deficiency results in substantial losses in crop yields. Zinc is an essential micronutrient which means it is essential for plant growth and development. Although zinc requirements vary among crops, zinc leaf concentrations (on a dry matter basis) in the range 20 to 100 mg/kg are adequate for most crops. Deficiency in zinc might result in significant reduction in crop yields and quality. In fact, yield can even be reduced by over 20% before any visual symptoms of the deficiency occur. The mobility of zinc in plants varies, depending on its availability in the soil or growing media. Symptoms of zinc deficiency include one or some of the symptoms are: Stunting - reduced height, Interveinal chlorosis, Brown spots on upper leaves, distorted leaves, reduced tillering, reduction in leaf size. Zinc may also be used as nano particle form. The source of Zinc may be Zinc oxide, zinc sulphate, zinc lactate, zinc gluconate, zinc proteino-lacto gluconate.

Iron is also required for photosynthesis and chlorophyll synthesis in plants. Iron availability in soils determines the distribution of plant species in natural ecosystems and limits crop yield and nutritional quality. Iron is immobile within the plant, inadequate iron uptake results in stunted growth, interveinal chlorosis, and decreased fitness.

Like Iron and Zinc, various other micronutrients enlisted herein above, may also be used in the composition of the present invention.

Further, one or more of the active ingredients of the present granular insecticidal composition, can be encapsulated for various purposes, such as to increase the residual biological activity, or to reduce the acute toxicity, or to obtain a physical or chemically stable formulation. The purpose

determines whether the "free" active ingredients and the "release rate" are relevant properties of a specific product.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition; and

D) Micronutrients, present in the range of 0.01 to 20 %, by weight of the composition.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition;

D) Micronutrients, present in the range of 0.01 to 20 %, by weight of the composition and

E) one or more agrochemically acceptable excipients.

In yet another preferred embodiment, the present invention provides a synergistic controlled release granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition;

D) Micronutrients, present in the range of 0.01 to 20 %, by weight of the composition and
E) one or more agrochemically acceptable excipients.

In another preferred embodiment, micronutrients are present in the range of 0.01 to 20 % by weight of the composition.

The composition of the present invention in addition to active insecticidal ingredients and micronutrients, further comprises agrochemically acceptable excipients including but not limited to dispersant or dispersing agent, wetting agent, emulsifiers, anti-freezing agent, anti-foaming agent, adjuvants , fillers , anti-microbial or anti-bacterial agent , thickening agent, stabilizers.

In further embodiment of the present invention, the insecticidal composition of the present invention further comprises agrochemically acceptable excipients including but not limited to surfactant/dispersing agent, wetting agent, emulsifiers, anti-freezing agent, anti-foaming agent, adjuvants, filler, antimicrobial/anti-bacterial agent, thickening agent, sticking agents, binders, co-binders, curing agents, carriers, fillers, stabilizers, colouring agents, dyes and solvent or mixtures thereof. suspension aid, disintegrating agent, thickener, slow (controlled) releasing agents, quick coating agent, spreader, anti-caking agents, preservatives, buffering agents or mixtures thereof. Additional components may also be included, e.g., protective colloids, adhesives, thixotropic agents, penetration agents, stabilisers, sequestering agents. More generally, the active materials can be combined with any solid or liquid additive, which complies with usual formulation techniques.

In yet another embodiment of the present invention, the insecticidal composition is formulated as granular (GR) or Controlled release (CR) formulation.

According to an aspect of the present invention, there is provided a controlled-release type pesticide granules comprising A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; B) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition.

According to another aspect of the present invention, natural wax may also be added to the synergistic granular insecticidal composition.

According to another aspect of the present invention, there is provided a method of cultivating a crop using the controlled-release type pesticide granules and/or granular insecticidal composition.

In another embodiment of the present invention, the controlled release insecticidal granular composition provides prolonged release of actives to provide better insect control.

In another embodiment of the present invention, the present granular or controlled release insecticidal composition can be applied to a plant/crop by spraying, irrigating, dusting, broadcasting, pouring, mist blowing, soil mixing, foaming, spreading-on, drenching, dipping or drip irrigation. etc.

In yet another embodiment of the present invention, the present granular or controlled release insecticidal composition can be applied to various plants including but not limited to such as paddy, sugarcane, cotton, cabbage, pigeon pea, cauliflower, tobacco, tomatoes, chilli, brinjal, okra, potatoes, leafy vegetables, oil crops, soybean, ground nut, Bengal gram, black gram, red gram, chickpea, grapes, bitter gourd, flowering ornamentals vine crops, tea and fruit trees etc.

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.

Variations or modifications to the composition of this invention, within the scope of the invention, may occur to those skilled in the art upon reviewing the disclosure herein. Such variations or modifications are well within the spirit of this invention.

All technical and scientific terms used herein have the same meanings as commonly understood by someone ordinarily skilled in the art to which the present subject matter belongs.

The terminology used, in the present disclosure, is only for the purpose of explaining a particular embodiment and such terminology shall not be considered to limit the scope of the present disclosure.

As used in the present disclosure, the forms "a," "an," and "the" may be intended to include the plural forms as well, unless the context clearly suggests 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 terms "comprises," "comprising," "including," and "having," are open ended transitional phrases and therefore specify the presence of stated features, integers, steps, operations, elements, but do not forbid the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof. The particular order of steps disclosed in the method and process of the present disclosure is not to be construed as necessarily requiring their performance as described or illustrated. It is also to be understood that additional or alternative steps may be employed.

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" or "active" used herein refers to that component of the composition responsible for control and killing of insect pests.

The terms "plants" and "vegetation" include, but are not limited to, germinant seeds, emerging seedlings, plants emerging from vegetative propagules, and established vegetation.

The term "formulation" and "composition" as used herein conveys the same meaning and can be used interchangeably.

The term "synergistic", as used herein, refers to the combined action of two or more active agents blended together and administered conjointly that is greater than the sum of their individual effects.

The term "crop" shall include a multitude of desired crop plants or an individual crop plant growing at a locus.

"Bioactive amounts" as mentioned herein means that amount which, when applied for treatment of crops, is sufficient to give effect in such treatment for control and killing of insect pests.

The term "control" means to inhibit the ability of insect pests to survive, grow, feed and/or reproduce, or to limit the pests related damage or loss in crop plants.

The term "pests" used herein includes insect pests affecting the crops.

The term "health of a plant" or "plant health" is defined as a condition of the plant and/or its products. As a result of the improved health; yield, plant vigour, quality and tolerance to abiotic or biotic stress is increased. As a result, the health of a plant is increased even in the absence of pest pressure. Accordingly, in an especially preferred embodiment of the method according to the invention, the health of a plant is increased both in the presence and absence of biotic or abiotic stress factors.

In another preferred embodiment of the invention, the yield of the plants treated using the composition of the present invention, is increased.

The term "benefit: cost" refers to a ratio used in a cost-benefit analysis to summarize the overall relationship between the relative costs and benefits of a proposled composition. If a treatment has a benefit-cost ratio greater than 1.0, the treatment is expected to deliver a positive and better outcome.

A further indicator for the condition of the plant is the plant vigour. The plant vigour manifests in several aspects such as the general visual appearance. Improved plant vigour can be characterized, among others, by the following improved properties of the plant: improved vitality of the plant, improved plant growth, improved plant development, improved visual appearance, improved plant stand (less plant verse/lodging), improved emergence, enhanced root growth

and/or more developed root system, enhanced nodulation, in particular rhizobial nodulation, bigger leaf blade, bigger size, increased plant weight, increased plant height, increased tiller number, increased number of side shoots, increased number of flowers per plant, increased shoot growth, increased root growth (extensive root system), increased yield when grown on poor soils or unfavourable climate, enhanced photosynthetic activity (e.g. based on increased stomatal conductance and/or increased CO2 assimilation rate), increased stomatal conductance, increased CO2 assimilation rate, enhanced pigment content (e.g. chlorophyll content), earlier flowering, earlier fruiting, earlier and improved germination, earlier grain maturity, improved self-defence mechanisms, improved stress tolerance and resistance of the plants against biotic and abiotic stress factors such as fungi, bacteria, viruses, insects, heat stress, cold stress, drought stress, UV stress and/or salt stress, less non-productive tillers, less dead basal leaves, less input needed(such as fertilizers or water), greener leaves, complete maturation under shortened vegetation periods, less fertilizers needed, less seeds needed, easier harvesting, faster and more uniform ripening, longer shelf-life, longer panicles, delay of senescence, stronger and/or more productive tillers, better extractability of ingredients, improved quality of seeds (for being seeded in the following seasons for seed production), better nitrogen uptake, improved reproduction, reduced production of ethylene and/or the inhibition of its reception by the plant.

In another especially preferred embodiment of the invention, the plant vigour of the treated plant is increased. In another preferred embodiment of the invention, the plant vigour of the plants treated according to the method of the invention is increased synergistically.

The improvement of the plant vigour according to the present invention particularly means that the improvement of any one or several or all of the above mentioned plant characteristics are improved.

Another indicator for the condition of the plant is the “quality” of a plant and/or its products.

In an especially preferred embodiment of the invention, the quality of the treated plant is increased.

In another preferred embodiment of the invention, the quality of the plants treated according to the method of the invention, is increased synergistically.

According to the present invention, enhanced quality means that certain plant characteristics such as the content or composition of certain ingredients are increased or improved by a measurable or noticeable amount over the same factor of the plant produced under the same conditions. Enhanced quality can be characterized, among others, by following improved properties of the plant or its product: increased nutrient content, increased protein content, increased content of fatty acids,
increased metabolite content, increased carotenoid content, increased sugar content, increased amount of essential amino acids, improved nutrient composition, improved protein composition, improved composition of fatty acids, improved metabolite composition, improved carotenoid composition, improved sugar composition, improved amino acids composition, improved or optimal fruit colour, improved leaf colour, higher storage capacity, higher processability of the harvested products.

In another preferred embodiment of the invention, there is higher a benefit-cost ratio and is greater than 1.

The present invention provides a synergistic granular insecticidal composition comprising bioactive amounts of:
A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives;
B) Emamectin or its agrochemically acceptable salts, esters and derivatives and
C) Fipronil or its agrochemically acceptable salts, esters and derivatives

In another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:
A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;
B) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; and
C) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

C) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition; and

D) one or more agrochemically acceptable excipients.

In one another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) Chlorantraniliprole or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; and

C) Emamectin Benzoate, present in the range of 0.01 to 1% by weight of the composition.

In yet another preferred embodiment, the present invention provides a synergistic controlled release granular insecticidal composition comprising:

A) Chlorantraniliprole or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition; and

D) one or more agrochemically acceptable excipients.

In one another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) Chlorantraniliprole, present as 0.45% by weight of the composition;

B) Emamectin Benzoate, present as 0.18% by weight of the composition; and

C) Fipronil or its agrochemically acceptable salts, esters and derivatives, present as 0.5% by weight of the composition.

In yet another preferred embodiment, the present invention provides a synergistic granular insecticidal composition comprising:

A) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

B) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition;

C) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01 to 1% by weight of the composition; and

D) Micronutrients, present in the range of 0.01 to 20 %, by weight of the composition.

In another preferred embodiment, the anthranilic diamide insecticide in the present composition is Chlorantraniliprole.

In yet another preferred embodiment of the present invention, Chlorantraniliprole or its agrochemically acceptable salts, esters and derivatives, is preferably present as 0.45% by weight of the composition.

In yet another preferred embodiment of the present invention, Emamectin or its agrochemically acceptable salts, esters and derivatives including Emamectin Benzoate, is preferably present as 0.18% by weight of the composition.

In yet another preferred embodiment of the present invention, Fipronil or its agrochemically acceptable salts, esters and derivatives, is preferably present as 0.5% by weight of the composition.

In yet another preferred embodiment of the present invention, the synergistic granular insecticidal composition comprises natural wax, or a fatty acid trivalent metal salt or alcohol type wax, or mixture thereof. natural wax comprises one or more of animal natural wax, or plant natural wax.

In another preferred embodiment, the granular insecticidal composition comprises zinc and/or iron, wherein Zinc is selected from zinc sulphate heptahydrate $ZnSO_47H_2O$, zinc sulphate mono hydrate $ZnSO_4.H_2O$, chelated zinc as Zn-EDTA, zinc oxide, Zinc Lactate Gluconate, Zinc Poly flavonoid, and Iron is selected from ferrous sulphate, chelated iron as Fe-EDTA.

In another embodiment of the present invention, the zinc, salts, derivatives or nanoparticles are selected from zinc sulphate heptahydrate $ZnSO_4.7H_2O$, zinc sulphate mono hydrate $ZnSO_4.H_2O$, Zinc chloride, chelated zinc as Zn-EDTA, zinc oxide, Zinc Lactate Gluconate, Zinc Poly flavonoid and zinc nano particles.

In another preferred embodiment, micronutrients are present in the range of 0.01 to 20 % by weight of the composition.

When the controlled-release type insecticide granules of the present invention includes the insecticidal active ingredient in a content ratio within the above range, a sufficient insect pest and weed control may be obtained and also a release control of the insecticidal active ingredient may be effectively achieved.

Meanwhile, the controlled-release type insecticide granules of the present invention may further include a coating layer containing natural wax on the entirety or part of the surface of the granules due to melting of the natural wax component in the pesticide granules, and in this case, during a predetermined release restraining period, there may be an advantage in that the leakage of some insecticide active ingredients into the environment is further restrained.

The granular insecticidal composition including the controlled-release type insecticide granules of the present invention have a time-release control type sustained release function and has an excellent time-release function in which leakage of the insecticidal active ingredient in the release restraining period is remarkably restrained. Therefore, in case the present invention is used, an ideal labor-saving pest control method may be realized in agricultural work.

In addition, the present invention may provide a method of cultivating crops using the granular insecticidal composition including the controlled-release type pesticide granules.

Crops to which the composition of present invention is applied but is not particularly limited to rice, paddy, cotton, chilli , sugarcane, leafy vegetables such as cabbage, Cauliflower, lettuce, spinach, brinjal and the likes, root vegetables such as radish, carrot, onion, tomato, cucumber, pumpkin, bitter gourd, and the likes, corns, potatoes, okra (bhindi), legumes including red gram (arhar/tur), pigeon pea, chickpea, bengal gram, black gram, soybean, industrial crops, grapes , tea, flowers, and the likes.

The present invention includes within its scope, all possible salts, esters and derivatives of the active ingredients of the composition.

In further embodiment of the present invention, the insecticidal composition of the present invention further comprises agrochemically acceptable excipients including but not limited to surfactant/dispersing agent, wetting agent, emulsifiers, anti-freezing agent, anti-foaming agent, adjuvants, filler, antimicrobial/anti-bacterial agent, thickening agent, sticking agents, binders, co-binders, curing agents, carriers, fillers, stabilizers, colouring agents, dyes and solvent , suspension aid, disintegrating agent, thickener, slow (controlled) releasing agents, quick coating agent, spreader, anti-caking agents, preservatives, buffering agents or mixtures thereof. Additional components may also be included, e.g., protective colloids, adhesives, thixotropic agents, penetration agents, stabilisers, sequestering agents. More generally, the active materials can be combined with any solid or liquid additive, which complies with usual formulation techniques.

A dispersant is a substance which adsorbs onto the surface of particles and helps to preserve the state of dispersion of the particles and prevents them from re-aggregating. Dispersants are added to agrochemical formulations to facilitate dispersion and suspension during manufacture, and to ensure the particles re-disperse into water in a spray tank. They are widely used in wettable powders, suspension concentrates and water-dispersible granules. Surfactants that are used as dispersants have the ability to adsorb strongly onto a particle surface and provide a charged or steric barrier to re-aggregation of particles. Examples of dispersing agent used herein but not limited to Calcium lignosulphonate, Alkyl aryl ether phosphate, tristyryl phenol ethoxylated Acrylic Copolymer/ Ethoxylated Tristryl phenol Sulphate, Naphthalene sulfonic acid, sodium salt condensate with formaldehyde, Ethoxylated oleyl cetyl alcohol, Alkyl aryl sulfonate,

Polyalkelene glycol ether, Ethoxylated Fatty alcohol or mixtures thereof and present in the range of 0.5-10% weight of the composition.

A wetting agent is a substance that when added to a liquid increases the spreading or penetration power of the liquid by reducing the interfacial tension between the liquid and the surface on which it is spreading. Wetting agents are used for two main functions in agrochemical formulations: during processing and manufacture to increase the rate of wetting of powders in water to make concentrates for soluble liquids or suspension concentrates; and during mixing of a product with water in a spray tank or other vessel to reduce the wetting time of wettable powders and to improve the penetration of water into water-dispersible granules. Examples of wetting agent used herein include but not limited to Tristyrylphenol ethoxylate, nonionic emulsifier/ Mixture of non-ionic surfactants & Alkoxylated Alcohol/Block copolymer, sodium lauryl sulphate; sodium dioctylsulphosuccinate; alkyl phenol ethoxylates; and aliphatic alcohol ethoxylates or mixtures thereof and present in the range of 0.5-10% weight of the composition.

Emulsifiers are molecules that stabilize emulsions, which are mixtures of immiscible liquids like oil and water. They work by reducing surface tension between the liquids, allowing them to mix uniformly and form a stable dispersion. Examples of emulsifiers as used herein include but not limited to Ionic and Anionic salts of emulsifiers. Emulseifiers used herein include but not limited to calcium alkyl benzene sulfonate, calcium hydroxyapatite, Potassium Dihydrogen Phosphate, Sodium Hydroxide, carbonated apatite, calcium carbonate, sodium bicarbonate, tricalcium phosphate, calcium phosphates, carbonated calcium phosphates, amine monomers, lactate dehydrogenase and magnesium hydroxide. Emulsifier are further added to Oil Dispersion formulations for uniform emulsions and are selected from Castor oil ethoxylates, modified naphthalene sulphonic acid condensate sodium salt, Acrylate copolymer, polyalkoxylated butyl ether, phenyl naphthalene sulphonates, ethoxylated alkyl phenols, ethoxylated fatty acids, alkoxylated linear alcohols, glyceryl esters, maleic anhydride co-polymers, condensation product of aryl sulphonic acids, addition product of ethylene oxide and fatty acid esters, lignin derivatives, naphthalene formaldehyde condensates, sodium salts of iso-decylsulfosuccinic acid half ester, Blend of modified poly ethanoxy ether and sulphated anionic surfactant, blend of alcohol alkoxylates & methyl methacrylate polymer, blend of di alkyl ate naphthalene sulphonic acid sodium salt, sodium alkyl benesulfonates, sodium salts of sulfonates naphthalene,

ammonium salts of Sulfonated naphthalene, salts of poly acrylic acids, salts of phenol Sulfonic acid and salts of naphthalene Sulfonic acids or mixtures thereof and present in the range of 0.1-10% weight of the total composition.

Carriers in agrochemical formulations are inert substances that serve as a medium to deliver active ingredients to target plants effectively. They enhance dispersion, adhesion, and absorption of the active ingredients, ensuring uniform application and optimal efficacy. Common carriers include solvents, surfactants, and inert powders tailored to specific formulation requirements. Carriers and/or fillers used herein include but not limited to talcum powder, clays, natural or synthetic silicates, silica, resins, waxes, solid fertilizers, Sand, Silicon Dioxide, China –Clay, Kaolin, Talc, starch or mixtures thereof and is present in the range of 0.1-90% weight of the total composition.

Binders and co-binders are substances that help hold the ingredients together, ensuring uniform distribution and adhesion to plant surfaces. Binders provide cohesion, while co-binders enhance adhesive properties and stability. They contribute to the effectiveness and longevity of the formulation, ensuring proper application and efficacy. Examples of Binders and Co-binders used herein include but not limited to poly-ethylene wax**,** poly vinyl alcohol, polyesters, polyamides, poly- carbonates, polyurea and polyurethanes, acrylate polymers and copolymers, styrene copolymers, butadiene copolymers, polysaccharides such as starch and cellulose derivatives, polymer of vinyl alcohol, vinyl acetate and vinyl pyrrolidone polymers and copolymers, polyethers, epoxy, phenolic and melamine resins, polyolefins and copolymers mixtures thereof. Examples of preferred polymers are acrylate polymers such as poly(methacrylate), poly (ethyl methacrylate), poly (methyl methacrylate), acrylate copoylmers and styrene-acrylic copolymers or mixtures thereof and is present in the range of 0.1-10% weight of the composition.

Curing agents are additives that facilitate the formation of stable, long-lasting films or coatings on plant surfaces after application. They promote adhesion, enhance durability, and improve resistance to environmental factors such as sunlight and water. Curing agents ensure effective protection and sustained efficacy of the agrochemical treatment. Examples of curing agent used herein include but not limited to modified starches, polyacrylates, sodium polyacrylate ,

polyvinyl alcohol and polyethylene oxide or mixtures thereof and is present in the range of 0.1-10% weight of the total composition.

Anti-foaming agents are substances that prevent or reduce the formation of foam in liquids by breaking down or inhibiting foam bubbles. The antifoaming agent may enable the wetting agent and the dispersant, when included, to function properly within the mixture, and may facilitate spraying of the insecticide while reducing the chances of the sprayer becoming clogged with foam or entrained air. Examples of anti-foaming agent as used herein include but not limited to silicon emulsion based anti-foam agents, Siloxane polyalkyleneoxide, trisiloxane ethoxylates, silicone oil, silicone compound, C10～C20 saturated fat acid compounds or C8～C10 aliphatic alcohols compound, silicone antifoam emulsion, dimethylsiloxane, polydimethyl siloxane emulsion, vegetable oil based antifoam, tallow based fatty acids, polyalkyleneoxide modified polydimethylsiloxane and mixtures thereof and present in the range of 0.01-3% weight of the total composition.

Anti-freezing agents are additives used to prevent freezing or crystallization of the product at low temperatures. They lower the freezing point of the solution, allowing it to remain in a liquid state even in cold environments. This ensures the effectiveness and stability of the agrochemical product during storage and application. Examples of anti-freezing agent as used herein include but not limited to Glycol, Propylene Glycol, Mono ethylene glycol, Glycerin, Diethylene glycol and present in the range of 0.1-20% weight of the composition.

Adjuvants as used herein include but not limited to Silicone Ethoxylated Oil, Polyvinyl Pyrrolidone, Poly vinyl Alcohol, Blend of poly terpene resin, Polyethylene Wax and present in the range of 0.1-10% weight of the composition.

Curing agent as used herein include but not limited to Sodium Polyacrylate (Sokalan PA 25 CL)

Fillers used herein but not limited to Silicon Dioxide, China –Clay, Kaolin, Talc, starch and is present in the range of 0.1-80% weight of the composition.

Anti-microbial or Anti-bacterial agent used herein include but not limited to Benzisothiazolin-3-one, Formaldehyde, Sodium benzoate, Sodium o-phenyl phenate, 5-chloro-2-methyl-4-

isothiazolin-3-one & 2-methyl-4-isothiazolin-3-one, Potassium sorbate or mixtures thereof and is present in the range of 0.01-5% weight of the composition.

Thickeners used herein include but not limited to Polysaccharides, carboxymethyl cellulose, Bentonite Clay, Aluminum Magnesium Silicate, Hydroxy propyl cellulose or mixtures thereof and is present in the range of 0.01-10% weight of the composition.

Stabilizers used herein but not limited to Epoxidised Vegetable Oil and is present in the range of 0.1-10 % weight of the composition.

The solvent for the formulation of the present invention may include heavy aromatic hydrocarbon, N methyl pyrollidone, Di methyl sulfoxide, N- alcohol, Alkyl amide, Vegetable Oil, Mineral Oil, Aromatic Solvents water, water-soluble alcohols and dihydroxy alcohol ethers. The water-soluble alcohol which can be used in the present invention may be lower alcohols or water-soluble macromolecular alcohols. The term “lower alcohol", as used herein, represents an alcohol having 1-4 carbon atoms, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, tert-butanol, etc. Macromolecular alcohol is not limited, as long as it may be dissolved in water in a suitable amount range, e.g., polyethylene glycol, sorbitol, glucitol, etc. The examples of suitable dihydroxy alcohol ethers used in the present invention may be dihydroxy alcohol alkyl ethers or dihydroxy alcohol aryl ethers. The examples of dihydroxy alcohol alkyl ether include ethylene glycol methyl ether, diethylene glycol methyl ether, propylene glycol methyl ether, dipropylene glycol methyl ether, ethylene glycol ethyl ether, diethylene glycol ethyl ether, propylene glycol ethyl ether, dipropylene glycol ethyl ether, etc. The examples of dihydroxy alcohol aryl ethers include ethylene glycol phenyl ether, diethylene glycol phenyl ether, propylene glycol phenyl ether, propylene glycol phenyl ether, and the like. Any of the above mentioned solvent can be used either alone or in combination thereof.

The synergistic composition of present invention can be applied to any and all developmental stages of pests, such as egg, larva, pupa, and adult. The pests may be controlled by contacting the target pest, its food supply, habitat, breeding ground or its locus with a pesticidally effective amount of the inventive mixtures or of compositions comprising the mixtures.

The inventive composition of present invention is highly effective in controlling insect pests, including but not limited to Boll worms, American bollworm, Spotted bollworm, Fruit & Shoot

Borer, Diamond back moth, Tobacco caterpillar, Termite, Fruit borer, Thrips, Mites, Pod borer, Thrips, Tea looper, Leaf folder, Hispa, Green semi looper, pod borer, Girdle beetle & Tobacco, caterpillar, Diamond Back Moth (Plutella xylostella) Fruit borer(Spodoptera litura & Helicoverpa armigera), Fruit borer (Spodoptera litura & Helicoverpa armigera) Thrips (Scritothrips dorsalis), Mites (Polypagotarsone mus latus), Stem borer, Brown plant hopper, Green leaf hopper, Rice leafhopper, White Backed Plant Hopper Rice Gall midge, Whorl maggot, White backed plant hopper, Aphid, Jassid, Thrips, White fly.

The composition according to the present invention can be applied to any and all developmental stages of insect pests, such as egg, nymph, larva, pupa, and adult. The insect pests may be controlled by contacting the target insect pest, habitat, breeding ground or its locus with a bioactive amount of the novel and inventive composition of the present invention.

In one embodiment, the composition according to the present invention acts synergistically to control insect pests in various crops.

In another embodiment, the composition according to present invention adopts a release control to provide prolonged release of actives thus providing better insect pests' control.

In another embodiment, the composition according to present invention provides good settle ability, basically no drift, little environmental pollution and no adverse effects on crops.

In another embodiment, the composition according to present invention, offers broad spectrum activity against various insect-pests.

In another embodiment, the composition according to present invention, shows high plant insects controlling effects against existing insects' resistant to chemicals, and no chemical damage against plants is observed.

In another embodiment, the composition according to present invention, is useful for treatment of plants and crops including but not limited to paddy, sugarcane, cotton, cabbage, pigeon pea, cauliflower, tobacco, tomatoes, chilli, brinjal, okra, potatoes, leafy vegetables, oil crops, soybean, ground nut, Bengal gram, black gram, red gram, chickpea, grapes, bitter gourd, flowering ornamentals vine crops, tea and fruit trees.

Representative examples of stable synergistic granular and controlled release insecticidal composition of the present invention, are provided as follows:

Table 1

EXAMPLE 1

Sr. No.	Ingredients	Percentage (%) W/W						
		E1	E2	E3	E4	E5	E6	E7
1	Chlorantraniliprole a.i.	0.01	1.00	0.45	0.30	0.30	0.45	0.30
2	Emamectin Benzoate a.i.	0.60	0.01	0.18	0.18	0.60	0.60	1.00
3	Fipronil a.i.	1.00	0.25	0.50	0.50	0.25	0.01	0.01
4	Calcium lignosulphonate	1.20	1.10	1.00	0.80	1.10	0.90	1.15
5	Emulsifier	0.50	0.40	0.20	0.10	0.20	0.10	4.00
6	Talcum Powder	10.00	8.00	7.75	5.00	7.75	6.00	8.50
7	Zinc Sulphate Monohydrate	1.50	1.50	1.50	1.50	1.50	1.50	1.50
8	Polyethylene Wax (PE wax)	0.50	0.50	0.50	0.50	0.50	0.50	0.50
9	Sodium Polyacrylate (Sokalan PA 25 CL)	0.60	0.50	0.40	0.20	0.40	0.30	0.40
10	Poly vinyl Alcohol (PVA)	0.10	0.10	0.10	0.10	0.10	0.10	0.10
11	Sand	83.99	86.64	87.42	90.82	87.30	89.54	82.54
	TOTAL	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

EXAMPLE 2

Sr. No.	Ingredients	Percentage (%) W/W
1	Chlorantraniliprole Technical	0.45 %
2	Emamectin Technical	0.18 %
3	Fipronil Technical	0.50 %
4	Calcium lignosulphonate	1.00 %
5	Emulsifier	0.20 %
6	Talcum Powder	7.75 %
7	Zinc Sulphate	0.50%
8	Polyethylene Wax (PE wax)	0.50 %
9	Sodium Polyacrylate (Sokalan PA 25 CL)	0.40 %
10	Poly vinyl Alcohol (PVA)	0.10 %
11	Sand	88.42 %
	TOTAL	100.00 %

Process: Charged the required quantity of filler/carriers, dispersing agent, zinc, & technicals of Chlorantraniliprole, Emamectin benzoate and Fipronil in premixing blender for homogenization for 30 minutes. Pre-blended material was then grinded through Jet mill/ air classifier mills. Finely grinded material was blended in post blender till it becomes homogeneous (approx. 1.5 hr). Homogeneous material was analysed. After getting approval from QC dept. material is unloaded into 25 kg. HDPE bag with LDPE liner inside. Further, charged the required quantity of sand in granulator. Added DM water, sticking agent and remaining material till it become homogeneous. Then added finely grinded material to completely coated on sand and mixed well. Final product was sent for QC approval. After approval material was packed in required pack sizes.

Stability Test:

Sr. No.	Test	Specification	Observation	14 days HST 54 °C
1.	Description	This material shall be in the form of blue color granules free from extraneous matter.	Complies	Complies
2	**Chlorantraniliprole** Content (% ,w/w)	0.45% (0.427% – 0.495%)	0.46	0.45
3	**Fipronil Content** (%, w/w)	0.50% (0.475% – 0.550%)	0.51	0.50
4	**Emamectin Content** (% ,w/w)	0.18% (0.171% - 0.198%)	0.19	0.18
5	Moisture by KF. (% ,w/w)	Max. 4.0	0.28	0.27
6	pH (1% Aqueous Solution)	6.0 - 8.50	7.32	7.28

BIO-EFFICACY AND SYNERGY DATA:

Evaluation of synergistic effect of insecticidal composition of the present invention

A synergistic effect of two or more products 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 two active components can be calculated as follows:

$$E = (X + Y) - \frac{XY}{100}$$

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

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

Where:

E represents expected percentage of pesticidal control for the combination of the two or three active ingredients at defined doses (for example equal to x, y and z, respectively).

X is the percentage of pesticidal control observed by the compound (Chlorantraniliprole) at a defined dose (equal to x).

Y is the percentage of pesticidal control observed by the compound (Emamectin benzoate) at a defined dose (equal to y).

Z is the percentage of pesticidal control observed by the compound (Fipronil) at a defined dose (equal to z).

When the percentage of pesticidal control observed for the combination is greater than the expected percentage, there is a synergism effect.

$$\text{Ratio} = \frac{\text{Observed control (\%)}}{\text{Expected control (\%)}}$$

Ratio of O/E > 1, synergism observed

The present invention is illustrated by way of examples, the examples are meant for illustrative purposes and should not be construed as limiting.

Experiment for Synergistic activity of composition of present invention:

Example 1- Details of experiment on paddy crop:

Field experiment for synergistic activity of Chlorantraniliprole belonging to diamide group (a stomach and contact insecticide), Emamectin benzoate belonging to avermectin group (a translaminar movement insecticide) and Fipronil belonging to phenylpyrozole group (a systemic stomach and contact insecticide) for the control of yellow stem borer (***Sciropophaga incertulas***) in paddy crop was conducted at farmer field, Raipur (Chhatisgarh).

To evaluate the synergistic effect, about one-month old paddy seedling (Variety: IET 4786) transplanted in 2 m x 3 m pilot plots maintaining 15 cm x 30 cm plant distance with three replications and in Randomized Block Design (RBD) during December 2021 to March, 2022. The granular treatments mentioned herein below were broadcasted in the field by mixing in sand 35 days after crop transplanting uniformly @ 10 kg/ha before initiation of pest incidence. The active components were applied at 6-7 doses in different ternary and binary combinations. Solo components were also taken for comparison. The treatment details are as under:

T1 – Chlorantraniliprole + Emamectin benzoate + Fipronil (0.01%+0.60%+1.00%)
T2 – Chlorantraniliprole + Emamectin benzoate + Fipronil (1.00%+0.01%+0.25%)
T3 – Chlorantraniliprole + Emamectin benzoate + Fipronil (0.45%+0.18%+0.50%)
T4 – Chlorantraniliprole + Emamectin benzoate + Fipronil (0.30%+0.18%+0.50%)
T5 – Chlorantraniliprole + Emamectin benzoate + Fipronil (0.30%+0.60%+0.25%)
T6 – Chlorantraniliprole + Emamectin benzoate + Fipronil (0.45%+0.60%+0.01%)
T7 – Chlorantraniliprole + Emamectin benzoate + Fipronil (0.30%+1.00%+0.01%)
T8 – Chlorantraniliprole + Emamectin benzoate (0.01%+0.60%)
T9 – Chlorantraniliprole + Emamectin benzoate (1.00%+0.01%)
T10 – Chlorantraniliprole + Emamectin benzoate (0.45%+0.18%)
T11 – Chlorantraniliprole + Emamectin benzoate (0.30%+0.18%)
T12 – Chlorantraniliprole + Emamectin benzoate (0.30%+0.60%)
T13 – Chlorantraniliprole + Emamectin benzoate (0.45%+0.60%)
T14 – Chlorantraniliprole + Emamectin benzoate (0.30%+1.00%)
T15 – Chlorantraniliprole + Fipronil (0.01%+1.00%)
T16 – Chlorantraniliprole + Fipronil (1.00%+0.25%)
T17 – Chlorantraniliprole + Fipronil (0.45%+0.50%)

T18 – Chlorantraniliprole + Fipronil (0.30%+0.50%)
T19 – Chlorantraniliprole + Fipronil (0.30%+0.25%)
T20 – Chlorantraniliprole + Fipronil (0.45%+0.01%)
T21 – Chlorantraniliprole + Fipronil (0.30%+0.01%)
T22 – Emamectin benzoate + Fipronil (0.60%+1.00%)
T23 – Emamectin benzoate + Fipronil (0.01%+0.25%)
T24 – Emamectin benzoate + Fipronil (0.18%+0.50%)
T25 – Emamectin benzoate + Fipronil (0.60%+0.25%)
T26 – Emamectin benzoate + Fipronil (0.60%+0.01%)
T27 – Emamectin benzoate + Fipronil (1.00%+0.01%)
T28 – Chlorantraniliprole (0.01%)
T29 – Chlorantraniliprole (1.00%)
T30 – Chlorantraniliprole (0.45%)
T31 – Chlorantraniliprole (0.30%)
T32 – Emamectin benzoate (0.60%)
T33 – Emamectin benzoate (0.01%)
T34 – Emamectin benzoate (0.18%)
T35 – Emamectin benzoate (1.00%)
T36 – Fipronil (1.00%)
T37 – Fipronil (0.25%)
T38 – Fipronil (0.50%)
T39 - Fipronil (0.01%)
T40 – Untreated check

The treatments T1 to T39 were applied as broadcasting by mixing in sand and in T40 control treatment only sand was applied. The application was done by hand wearing rubber gloves. The observations for dead hearts caused due to the incidence of yellow stem borer were recorded at 15 and 30 days after treatment application by observing the random 100 tillers per replicated plot.

Based on the data recorded per cent reduction in dead hearts calculated over control. Further based on the per cent reduction in dead hearts at 15 and 30 days after treatment application, the **Expected control** was calculated and compared with **Observed control**. The results of the trial have been presented here under in Table 1 and 2.

Table 1: Synergistic effect of combination product of the present invention (Chlorantraniliprole + Emamectin benzoate + Fipronil) against yellow stem borer in paddy crop 15 days after treatment application

S. No.	Treatment	Formulation	Observed per cent control	Expected per cent control	Colby Ratio
T1	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.01%+0.60% +1.00%	93.27	74.68	**1.249**
T2	Chlorantraniliprole + Emamectin benzoate + Fipronil	1.00%+0.01% +0.25%	94.23	72.69	**1.296**
T3	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.45%+0.18% +0.50%	99.04	73.68	**1.344**
T4	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.30%+0.18% +0.50%	92.31	71.15	**1.297**
T5	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.30%+0.60% +0.25%	86.54	73.01	**1.185**
T6	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.45%+0.60% +0.01%	92.31	72.30	**1.277**
T7	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.30%+1.00% +0.01%	75.00	70.05	**1.071**
T8	Chlorantraniliprole + Emamectin benzoate	0.01%+0.60%	33.66	52.12	**0.646**
T9	Chlorantraniliprole + Emamectin benzoate	1.00%+0.01%	54.81	60.55	**0.905**
T10	Chlorantraniliprole + Emamectin benzoate	0.45%+0.18%	51.93	57.22	**0.908**
T11	Chlorantraniliprole + Emamectin benzoate	0.30%+0.18%	46.16	53.11	**0.869**
T12	Chlorantraniliprole + Emamectin benzoate	0.30%+0.60%	48.08	61.01	**0.788**
T13	Chlorantraniliprole + Emamectin benzoate	0.45%+0.60%	50.97	64.43	**0.791**
T14	Chlorantraniliprole + Emamectin benzoate	0.30%+1.00%	52.89	61.54	**0.859**
T15	Chlorantraniliprole + Fipronil	0.01%+1.00%	63.47	64.41	**0.985**
T16	Chlorantraniliprole + Fipronil	1.00%+0.25%	67.31	70.72	**0.952**
T17	Chlorantraniliprole + Fipronil	0.45%+0.50%	64.43	69.24	**0.931**
T18	Chlorantraniliprole + Fipronil	0.30%+0.50%	60.58	66.28	**0.914**
T19	Chlorantraniliprole + Fipronil	0.30%+0.25%	58.66	62.06	**0.945**
T20	Chlorantraniliprole + Fipronil	0.45%+0.01%	60.58	61.07	**0.992**
T21	Chlorantraniliprole + Fipronil	0.30%+0.01%	49.04	57.32	**0.856**
T22	Emamectin benzoate + Fipronil	0.60%+1.00%	52.89	62.38	**0.848**
T23	Emamectin benzoate + Fipronil	0.01%+0.25%	27.89	35.44	**0.787**
T24	Emamectin benzoate + Fipronil	0.18%+0.50%	35.58	47.35	**0.752**
T25	Emamectin benzoate + Fipronil	0.60%+0.25%	34.62	50.75	**0.682**
T26	Emamectin benzoate + Fipronil	0.60%+0.01%	30.78	44.59	**0.690**
T27	Emamectin benzoate + Fipronil	1.00%+0.01%	23.08	45.34	**0.509**
T28	Chlorantraniliprole	0.01%	32.70	-	**-**

T29	Chlorantraniliprole	1.00%	57.70	-	-
T30	Chlorantraniliprole	0.45%	50.00	-	-
T31	Chlorantraniliprole	0.30%	45.20	-	-
T32	Emamectin benzoate	0.60%	28.85	-	-
T33	Emamectin benzoate	0.01%	6.74	-	-
T34	Emamectin benzoate	0.18%	14.43	-	-
T35	Emamectin benzoate	1.00%	29.81	-	-
T36	Fipronil	1.00%	47.12	-	-
T37	Fipronil	0.25%	30.78	-	-
T38	Fipronil	0.50%	38.47	-	-
T39	Fipronil	0.01%	22.12	-	-
T40	Control	-	-	-	-

Table 2: Synergistic effect of composition of the present invention (Chlorantraniliprole + Emamectin benzoate + Fipronil) against yellow stem borer in paddy crop 30 days after treatment application

S. No.	Treatment	Formulation	Observed per cent control	Expected per cent control	Colby Ratio
T1	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.01%+0.60% +1.00%	84.68	71.04	**1.192**
T2	Chlorantraniliprole + Emamectin benzoate + Fipronil	1.00%+0.01% +0.25%	94.35	69.08	**1.366**
T3	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.45%+0.18% +0.50%	97.58	68.73	**1.420**
T4	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.30%+0.18% +0.50%	92.74	66.50	**1.395**
T5	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.30%+0.60% +0.25%	87.10	67.42	**1.292**
T6	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.45%+0.60% +0.01%	92.74	65.54	**1.415**
T7	Chlorantraniliprole + Emamectin benzoate + Fipronil	0.30%+1.00% +0.01%	75.80	64.68	**1.172**
T8	Chlorantraniliprole + Emamectin benzoate	0.01%+0.60%	38.70	52.13	**0.743**
T9	Chlorantraniliprole + Emamectin benzoate	1.00%+0.01%	45.96	57.40	**0.801**
T10	Chlorantraniliprole + Emamectin benzoate	0.45%+0.18%	43.54	54.92	**0.793**
T11	Chlorantraniliprole + Emamectin benzoate	0.30%+0.18%	41.12	51.70	**0.795**
T12	Chlorantraniliprole + Emamectin benzoate	0.30%+0.60%	41.93	55.12	**0.761**
T13	Chlorantraniliprole + Emamectin benzoate	0.45%+0.60%	45.16	58.11	**0.777**
T14	Chlorantraniliprole + Emamectin benzoate	0.30%+1.00%	44.35	57.07	**0.777**
T15	Chlorantraniliprole + Fipronil	0.01%+1.00%	49.19	60.97	**0.807**

T16	Chlorantraniliprole + Fipronil	1.00%+0.25%	54.03	65.46	**0.825**
T17	Chlorantraniliprole + Fipronil	0.45%+0.50%	49.19	60.84	**0.808**
T18	Chlorantraniliprole + Fipronil	0.30%+0.50%	47.58	58.04	**0.820**
T19	Chlorantraniliprole + Fipronil	0.30%+0.25%	46.77	56.09	**0.834**
T20	Chlorantraniliprole + Fipronil	0.45%+0.01%	49.19	53.56	**0.918**
T21	Chlorantraniliprole + Fipronil	0.30%+0.01%	41.93	50.24	**0.835**
T22	Emamectin benzoate + Fipronil	0.60%+1.00%	33.87	55.12	**0.614**
T23	Emamectin benzoate + Fipronil	0.01%+0.25%	22.57	35.02	**0.645**
T24	Emamectin benzoate + Fipronil	0.18%+0.50%	26.61	44.62	**0.596**
T25	Emamectin benzoate + Fipronil	0.60%+0.25%	27.41	46.14	**0.594**
T26	Emamectin benzoate + Fipronil	0.60%+0.01%	26.61	38.96	**0.683**
T27	Emamectin benzoate + Fipronil	1.00%+0.01%	20.15	41.61	**0.484**
T28	Chlorantraniliprole	0.01%	35.48	-	**-**
T29	Chlorantraniliprole	1.00%	52.42	-	**-**
T30	Chlorantraniliprole	0.45%	43.54	-	**-**
T31	Chlorantraniliprole	0.30%	39.51	-	**-**
T32	Emamectin benzoate	0.60%	25.80	-	**-**
T33	Emamectin benzoate	0.01%	10.48	-	**-**
T34	Emamectin benzoate	0.18%	20.15	-	**-**
T35	Emamectin benzoate	1.00%	29.03	-	**-**
T36	Fipronil	1.00%	39.51	-	**-**
T37	Fipronil	0.25%	27.41	-	**-**
T38	Fipronil	0.50%	30.64	-	**-**
T39	Fipronil	0.01%	17.74	-	**-**
T40	Control	-	-	-	**-**

It is clearly evident from the data shown in Table 1 and 2 for per cent reduction in dead hearts due to yellow stem borer incidence in paddy crop that the ternary composition of the present invention comprising Chlorantraniliprole, Emamectin benzoate and Fipronil T1 to T7 are highly synergistic in each case with > 1 Colby's Ratio. The binary combination of two products Chlorantraniliprole + Emamectin benzoate (T8 to T14), Chlorantraniliprole + Fipronil (T15 to T21) and Emamectin benzoate + Fipronil (T22 to T27) are compatible but antagonistic effect shown for the control of dead hearts as compared to ternary combination of Chlorantraniliprole, Emamectin benzoate and Fipronil. The binary combinations of any two insecticides (T8 to T27) are thus less effective to control yellow stem borer incidence in terms of dead hearts as compared to ternary combination of three insecticides Chlorantraniliprole + Emamectin benzoate + Fipronil (T1 to T7).

Experiment for Bio-efficacy evaluation of composition of present invention:

For the bio-efficacy evaluation of ternary composition based on Chlorantraniliprole belonging to diamide group (a stomach and contact insecticide), Emamectin benzoate belonging to avermectin group (a translaminar movement insecticide) and Fipronil belonging to phenylpyrozole group (a systemic stomach and contact insecticide) under field conditions for the control of yellow stem borer (*Sciropophaga incertulas*) and leaf folder (*Cnaphalocrosis medinalis*) in paddy crop, a field experiment was conducted at farmer field, Sonipat (Haryana). The ternary granular treatments comprising different composition based on Chlorantraniliprole 0.01, 0.30, 0.45 and 1.00%, Emamectin benzoate 0.01, 0.18, 0.60 and 1.00% and Fipronil 0.01, 0.25, 0.50 and 1.00% were evaluated under field conditions @ 10 kg/ha. For comparison granular formulations of the ternary product components available in the market Chlorantraniliprole 0.4% GR, Fipronil 0.6% GR and a combo product based on Emamectin benzoate (Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR) and another standard treatment Flubendiamide 0.70% GR were also included in the treatment schedule and applied at respective approved dose rates.

Example 2: Bio-efficacy evaluation of the composition of the present invention on paddy crop

For the bio-efficacy evaluation of ternary combination products under field conditions based on different active ingredients of Chlorantraniliprole, Emamectin benzoate and Fipronil specifically manufactured by the inventor for the control of yellow stem borer (*Sciropophaga incertulas*) and leaf folder (*Cnaphalocrosis medinalis*) in paddy crop, an experiment was conducted at farmer field, Sonipat (Haryana) during July to October, 2022. About one-month old paddy seedling (Variety: IR-1121, Pusa Sugandha-4) were transplanted in 4 m x 5 m plots maintaining 15 cm x 30 cm plant distance with three replications and following Randomized Block Design (RBD). The granular ternary all the treatments were broadcasted in the field by mixing in sand 35 days after crop transplanting uniformly @ 10 kg/ha before initiation of pest incidence by hand wearing rubber gloves. For comparison, granular formulations of the ternary product components available in the market Chlorantraniliprole 0.40% GR, Fipronil 0.60% GR and a combo product based on Emamectin benzoate (Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR) and another standard treatment Flubendiamide 0.70% GR were also applied at respective approved dose rates.

The observations were recorded for the following objectives.

Objectives:

1. Bio-efficacy evaluation against stem borer incidence based on per cent dead hearts in paddy crop
2. Bio-efficacy evaluation against stem borer incidence based on per cent white ear heads in paddy crop
3. Bio-efficacy evaluation against leaf folder incidence based on percent leaf damaged in paddy crop
4. Bio-efficacy evaluation based on per cent reduction in dead hearts due to stem borer over untreated control
5. Bio-efficacy evaluation based on per cent reduction in white ear heads due to stem borer over untreated control
6. Bio-efficacy evaluation based on per cent reduction in leaf damage due to leaf folder over untread control
7. Bio-efficacy evaluation based on paddy yield
8. Effect on natural enemies in paddy crop ecosystem
9. Phytotoxicity evaluation on paddy crop
10. Economics of treatments based on Cost: Benefit Ratio

Treatment details:

T1 – Chlorantraniliprole 0.01% + Emamectin benzoate 0.60% + Fipronil 1.00% GR @ 10 kg/ha
T2 – Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR @ 10 kg/ha
T3 – Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha
T4 – Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha
T5 – Chlorantraniliprole 0.30% + Emamectin benzoate 0.60% + Fipronil 0.25% GR @ 10 kg/ha
T6 – Chlorantraniliprole 0.45% + Emamectin benzoate 0.60% + Fipronil 0.01% GR @ 10 kg/ha
T7 – Chlorantraniliprole 0.30% + Emamectin benzoate 1.00% + Fipronil 0.01% GR @ 10 kg/ha
T8 – Fipronil 0.60% GR @ 10 kg/ha
T9 – Chlorantraniliprole 0.40% GR @ 10 kg/ha
T10 – Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR @ 7.5 kg/ha
T11 – Flubendiamide 0.70% GR @ 14.28 kg/ha
T12 – Untreated control

Methodology:

The treatments T1 to T11 were broadcasted after mixing in equal quantity of sand as per farmers practice, and in T12 control treatment only sand was applied 35 days after crop transplanting. The observations for yellow stem borer incidence in terms of dead hearts were recorded at 15 and 30 days after treatment application based on randomly selected 100 tillers per plot. The white ear heads due to the incidence of yellow stem borer were also recorded at crop harvest. The incidence of leaf folder was recorded in terms of per cent leaf damaged based on randomly selected 100 leaves per plot at 15, 30 and 45 days after treatment application.

Based on the data recorded per cent reduction in dead hearts, white ear heads and leaf damaged were calculated over control. The crop yield was recorded plot wise at harvest and expressed as q/ha. The observations for impact of treatments on natural enemies were recorded before application of treatments and at 15 and 30 days after application. The phytotoxicity symptoms (leaf injury on tips/ surface, wilting, vein clearing, stunting, chlorosis, necrosis, epinasty and hyponasty) on paddy crop were recorded visually at 10, 15, 20 and 30 days after treatment application. Based on treatment application cost, market price of produce and net profit, the Cost: Benefit Ratio was calculated for the economics of treatments. The data were subjected to statistically analysis of variance. Results are presented in Tables 3 to 7.

Results:

The results for per cent dead hearts at 15 and 30 days after treatment application and per cent white ear heads at crop harvest due to the incidence of yellow stem borer and per cent reduction in dead hearts and white ear heads over control are summarized in Table 3. The data on per cent leaf damaged at 15, 30 and 45 days after treatment application due to the incidence of leaf folder and per cent reduction in leaf damaged over control are summarized in Table 4. The paddy grain yield data recorded at crop harvest and Cost: Benefit Ratio calculated is presented in Table 5. The observations recorded for natural enemies (spiders and coccinellids) and phytotoxicity symptoms are presented in Tables 6 and 7, respectively.

Table 3: Bio-efficacy evaluation of different ternary combination of Chlorantraniliprole, Emamectin benzoate and Fipronil against yellow stem borer incidence in paddy crop

S. No.	Treatment	Formulation dose (kg/ha)	DH at 15 DAA (%)	DH at 30 DAA (%)	WEH at harvest (%)	Per cent reduction over control		
						DH at 15 DAA	DH at 30 DAA	WEH at harvest
T1	Chlorantraniliprole 0.01% + Emamectin benzoate 0.60% + Fipronil 1.00% GR	10	7.00 (2.73)	11.33 (3.44)	5.00 (2.32)	66.67	69.91	75.41
T2	Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR	10	4.33 (2.20)	7.00 (2.72)	3.00 (1.86)	79.37	81.42	85.25
T3	Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	2.67 (1.77)	4.33 (2.19)	2.33 (1.68)	87.30	88.50	88.52
T4	Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	4.67 (2.26)	8.00 (2.91)	3.67 (2.03)	77.78	78.76	81.97
T5	Chlorantraniliprole 0.30% + Emamectin benzoate 0.60% + Fipronil 0.25% GR	10	6.33 (2.60)	10.67 (3.34)	4.33 (2.20)	69.84	71.68	78.69
T6	Chlorantraniliprole 0.45% + Emamectin benzoate 0.60% + Fipronil 0.01% GR	10	5.67 (2.48)	9.67 (3.19)	5.67 (2.47)	73.02	74.34	72.13
T7	Chlorantraniliprole 0.30% + Emamectin benzoate 1.00% + Fipronil 0.01% GR	10	8.00 (2.88)	14.33 (3.84)	7.33 (2.79)	61.90	61.95	63.93
T8	Fipronil 0.60% GR	10	10.33 (3.29)	17.67 (4.25)	8.00 (2.90)	50.79	53.10	60.66
T9	Chlorantraniliprole 0.40% GR	10	9.67 (3.18)	14.00 (3.80)	6.67 (2.67)	53.97	62.83	67.21
T10	Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR	7.5	11.00 (3.39)	19.67 (4.48)	9.67 (3.17)	47.62	47.79	52.46
T11	Flubendiamide 0.70% GR	14.28	7.33 (2.80)	10.33 (3.29)	6.00 (2.54)	65.08	72.57	70.49
T12	Untreated control	-	21.00 (4.63)	37.67 (6.17)	20.33 (4.56)	-	-	-
	S Em ±		0.15	0.16	0.17			
	CD (P=0.05)		0.43	0.48	0.51			

Figures in parentheses are square root transformed values (x + 0.5)
DH – Dead hearts WEH – White ear head DAA – Days after treatment application

Table 4: Bio-efficacy evaluation of different ternary combination of Chlorantraniliprole, Emamectin benzoate and Fipronil against leaf folder incidence in paddy crop

S. No.	Treatment	Formulation dose (kg/ha)	Per cent leaf damaged			Per cent reduction over control		
			15 DAA	30 DAA	45 DAA	15 DAA	30 DAA	45 DAA
T1	Chlorantraniliprole 0.01% + Emamectin benzoate 0.60% +	10	4.33	8.67	9.67	75.93	69.77	74.11

	Fipronil 1.00% GR		(2.20)	(3.03)	(3.19)			
T2	Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR	10	2.00 (1.56)	5.33 (2.41)	6.67 (2.67)	88.89	81.40	82.14
T3	Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	1.33 (1.34)	3.67 (2.04)	4.33 (2.19)	92.59	87.21	88.39
T4	Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	5.00 (2.34)	6.67 (2.68)	9.33 (3.13)	72.22	76.74	75.00
T5	Chlorantraniliprole 0.30% + Emamectin benzoate 0.60% + Fipronil 0.25% GR	10	6.33 (2.61)	8.33 (2.96)	11.33 (3.44)	64.81	70.93	69.64
T6	Chlorantraniliprole 0.45% + Emamectin benzoate 0.60% + Fipronil 0.01% GR	10	5.67 (2.48)	7.33 (2.79)	10.33 (3.29)	68.52	74.42	72.32
T7	Chlorantraniliprole 0.30% + Emamectin benzoate 1.00% + Fipronil 0.01% GR	10	6.67 (2.67)	10.67 (3.34)	14.33 (3.85)	62.96	62.79	61.61
T8	Fipronil 0.60% GR	10	11.33 (3.43)	15.33 (3.98)	16.67 (4.14)	37.04	46.51	55.36
T9	Chlorantraniliprole 0.40% GR	10	8.00 (2.91)	12.67 (3.63)	14.67 (3.89)	55.56	55.81	60.71
T10	Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR	7.5	10.33 (3.28)	14.33 (3.84)	16.33 (4.10)	42.59	50.00	56.25
T11	Flubendiamide 0.70% GR	14.28	8.33 (2.97)	11.67 (3.48)	13.67 (3.76)	53.70	59.30	63.39
T12	Untreated control	-	18.00 (4.29)	28.67 (5.40)	37.33 (6.15)	-	-	-
	S Em ±		0.15	0.13	0.12			
	CD (P=0.05)		0.43	0.39	0.36			

Figures in parentheses are square root transformed values (x + 0.5) DAA – Days after treatment application

Table 5: Bio-efficacy evaluation of different ternary combination of Chlorantraniliprole, Emamectin benzoate and Fipronil based on paddy yield and Cost: Benefit Ratio

S. No.	Treatment	Formulation dose (kg/ha)	Yield (q/ha)	Per cent increase in yield over control	Cost: Benefit Ratio
T1	Chlorantraniliprole 0.01% + Emamectin benzoate 0.60% + Fipronil 1.00% GR	10	37.47 (6.12)	43.55	1 : 2.33
T2	Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR	10	40.78 (6.39)	56.26	1 : 2.28
T3	Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	42.33 (6.51)	62.20	1 : 4.52
T4	Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	39.50 (6.28)	51.34	1 : 4.36
T5	Chlorantraniliprole 0.30% + Emamectin benzoate 0.60% + Fipronil 0.25% GR	10	37.27 (6.10)	42.78	1 : 2.58
T6	Chlorantraniliprole 0.45% + Emamectin benzoate 0.60% + Fipronil 0.01% GR	10	38.25 (6.18)	46.55	1 : 2.76
T7	Chlorantraniliprole 0.30% + Emamectin benzoate 1.00% + Fipronil 0.01% GR	10	36.82 (6.07)	41.06	1 : 1.80

T8	Fipronil 0.60% GR	10	32.22 (5.67)	23.44	1 : 2.06
T9	Chlorantraniliprole 0.40% GR	10	33.88 (5.82)	29.82	1 : 2.11
T10	Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR	7.5	31.73 (5.63)	21.58	1 : 1.14
T11	Flubendiamide 0.70% GR	14.28	35.27 (5.93)	35.12	1 : 2.21
T12	Untreated control	-	26.10 (5.11)	-	-
	S Em ±		0.10		
	CD (P=0.05)		0.30		

Figures in parentheses are square root transformed values

Table 6: Effect of different ternary combination of Chlorantraniliprole, Emamectin benzoate and Fipronil on natural enemies in paddy crop

S. No.	Treatment	Formulation dose (kg/ha)	Spiders/ hill			Coccinellids/ hill		
			Before application	Days after application		Before application	Days after application	
				15	30		15	30
T1	Chlorantraniliprole 0.01% + Emamectin benzoate 0.60% + Fipronil 1.00% GR	10	3.07 (1.89)	2.77 (1.81)	2.93 (1.85)	2.23 (1.65)	2.03 (1.58)	1.73 (1.49)
T2	Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR	10	2.80 (1.82)	2.60 (1.76)	2.73 (1.79)	1.97 (1.57)	2.17 (1.63)	1.93 (1.56)
T3	Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	2.83 (1.83)	2.80 (1.82)	2.60 (1.76)	2.07 (1.60)	1.73 (1.49)	2.07 (1.60)
T4	Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	2.93 (1.85)	3.17 (1.91)	2.80 (1.81)	2.17 (1.63)	2.23 (1.65)	1.77 (1.50)
T5	Chlorantraniliprole 0.30% + Emamectin benzoate 0.60% + Fipronil 0.25% GR	10	3.23 (1.93)	3.07 (1.89)	2.97 (1.86)	2.30 (1.67)	2.20 (1.64)	1.80 (1.51)
T6	Chlorantraniliprole 0.45% + Emamectin benzoate 0.60% + Fipronil 0.01% GR	10	2.70 (1.79)	2.77 (1.80)	2.63 (1.77)	2.27 (1.66)	2.10 (1.61)	2.17 (1.63)
T7	Chlorantraniliprole 0.30% + Emamectin benzoate 1.00% + Fipronil 0.01% GR	10	3.37 (1.97)	2.83 (1.82)	2.43 (1.71)	2.40 (1.70)	2.03 (1.59)	1.87 (1.54)
T8	Fipronil 0.60% GR	10	3.03 (1.88)	2.93 (1.85)	2.67 (1.78)	2.10 (1.61)	1.83 (1.52)	2.07 (1.60)
T9	Chlorantraniliprole 0.40% GR	10	3.27 (1.94)	2.77 (1.81)	2.40 (1.70)	2.20 (1.64)	1.97 (1.57)	1.90 (1.55)
T10	Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR	7.5	2.87 (1.83)	2.67 (1.78)	2.70 (1.79)	2.23 (1.65)	2.13 (1.62)	1.70 (1.48)
T11	Flubendiamide 0.70% GR	14.28	3.20 (1.92)	2.97 (1.86)	2.90 (1.84)	2.17 (1.63)	1.80 (1.51)	1.83 (1.53)
T12	Untreated control	-	3.10 (1.90)	2.93 (1.85)	2.77 (1.81)	2.37 (1.69)	2.00 (1.57)	2.03 (1.59)

	S Em ±		0.04	0.05	0.06	0.04	0.07	0.05
	CD (P=0.05)		NS	NS	NS	NS	NS	NS

Figures in parentheses are square root transformed values NS – Non significant

Table 7: Phytotoxicity evaluation of different ternary combination of Chlorantraniliprole, Emamectin benzoate and Fipronil on paddy crop

S. No.	Treatment	Formulation dose (kg/ha)	Phytotoxicity parameters observed* (mean data recorded at 10, 15, 20 and 30 days after application)							
			L	W	N	V	C	S	E	H
T1	Chlorantraniliprole 0.01% + Emamectin benzoate 0.60% + Fipronil 1.00% GR	10	0	0	0	0	0	0	0	0
T2	Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR	10	0	0	0	0	0	0	0	0
T3	Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	0	0	0	0	0	0	0	0
T4	Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR	10	0	0	0	0	0	0	0	0
T5	Chlorantraniliprole 0.30% + Emamectin benzoate 0.60% + Fipronil 0.25% GR	10	0	0	0	0	0	0	0	0
T6	Chlorantraniliprole 0.45% + Emamectin benzoate 0.60% + Fipronil 0.01% GR	10	0	0	0	0	0	0	0	0
T7	Chlorantraniliprole 0.30% + Emamectin benzoate 1.00% + Fipronil 0.01% GR	10	0	0	0	0	0	0	0	0
T8	Fipronil 0.60% GR	10	0	0	0	0	0	0	0	0
T9	Chlorantraniliprole 0.40% GR	10	0	0	0	0	0	0	0	0
T10	Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR	7.5	0	0	0	0	0	0	0	0
T11	Flubendiamide 0.70% GR	14.28	0	0	0	0	0	0	0	0
T12	Untreated control	-	0	0	0	0	0	0	0	0

Based on 0-10 scale where: 0=0%, 1=1-10%, 2=11-20%, 3=21-30%, 4=31-40%, 5=41-50%, 6=51-60%, 7=61-70%, 8=71-80%, 9=81-90%, 10=91-100%
L – Leaf injury on tips/surface, W – Wilting, N – Necrosis, V – Vein clearing, C – Chlorosis, S – Stunting, E – Epinasty H – Hyponasty

From the example, it can be clearly seen that the ternary composition of the present invention are superior for controlling the yellow stem borer incidence in terms of per cent dead hearts at 15 and 30 days after treatment application and also in terms of white ear heads at crop harvest (Table 3). Also, the percent leaf damaged by leaf folder at 15, 30 and 45 days after treatment application was effectively controlled by the ternary compositions of present invention as compared to solo formulations and other standard treatments. Thus, the effectiveness of ternary composition on paddy crop was superior over solo component comprising Chlorantraniliprole 0.40% GR, Fipronil 0.60% GR and a combo product of Emamectin benzoate with Cartap

hydrochloride (Cartap hydrochloride 7.5% + Emamectin benzoate 0.25% GR) applied at respective dosage levels. Other registered formulated product available in the market, Flubendiamide 0.70% GR evaluated was also less effective to ternary composition products. Amongst the ternary compositions, the treatment T3 (Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha) was most prominent to control yellow stem borer and leaf folder incidence in paddy crop followed by treatments T2 (Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR @ 10 kg/ha) and T4 (Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha) and these treatments were significantly superior to other ternary combination products.

The yield of paddy grains also improved in the ternary composition of Chlorantraniliprole, Emamectin benzoate and Fipronil as compared to other products (Table 5). One of the reasons of higher crop yield in ternary treatments may be due to better control of yellow stem borer and leaf folder damage resulting into increased number of productive tillers/hill. The Cost: Benefit Ratio revealed that ternary combination T3 (Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha) and T4 (Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha) were most economical with higher Cost: Benefit Ratio as compared to other ternary and already registered and available in market standard treatments (Table 5).

The disclosed composition of Chlorantraniliprole, Emamectin benzoate and Fipronil based granular formulations showed no adverse impact on the natural enemies (spiders and coccinellids) most prevailing in the paddy crop ecosystem being the population significantly at par with control and other treatments before treatments application and at 15 and 30 days after application (Table 6). Also, the ternary granular formulations based on Chlorantraniliprole, Emamectin benzoate and Fipronil showed no phytotoxicity to the paddy crop when observed at 10, 15, 20 and 30 days after treatment application (Table 7).

It is evident from the above tables of examples that the composition of the present invention Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha resulted in efficient control of yellow stem borer and leaf folder incidence and in increasing the crop yield as compared to the other ternary compositions and reference standard products (binary and solo products). The Cost: Benefit Ratio also showed that ternary composition of

Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha was most economical with higher Cost: Benefit Ratio as compared to other ternary and standard treatments. Further, the composition of present invention is resulted synergistic.

ADVANTAGES OF THE PRESENT INVENTION:

1. The synergistic granular composition of the present invention resulted in significantly higher per cent control of dead hearts and white ear heads due to yellow stem borer incidence and per cent leaf damaged by leaf folder and in increasing the overall growth of paddy crop and yield as compared to the standard treatments and untreated control.

2. Amongst the synergistic composition of the present invention, Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha, Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR @ 10 kg/ha and Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha were significantly superior over other ternary compositions and formulated products already available in the market in controlling the yellow stem borer incidence in terms of dead hearts at 15 and 30 days after treatment application and in terms of white ear heads at paddy crop harvest. Also, these treatments were superior in controlling leaf damage by leaf folder at 30, 45 and 60 days after treatment application.

3. The synergistic combination of the present invention viz., Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha, Chlorantraniliprole 1.00% + Emamectin benzoate 0.01% + Fipronil 0.25% GR @ 10 kg/ha and Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha provides improved yield as compared to the untreated control and other treatments applied in paddy crop. The treatments Chlorantraniliprole 0.45% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha and Chlorantraniliprole 0.30% + Emamectin benzoate 0.18% + Fipronil 0.50% GR @ 10 kg/ha were found most economical with higher Cost: Benefit Ratio.

4. The synergistic combinations show no adverse impact on natural enemies in paddy crop ecosystem and also no phytotoxic effect on the crop.

5. The results of experiments indicate that the synergistic composition of Chlorantraniliprole + Emamectin benzoate + Fipronil GR is highly effective in controlling yellow stem borer and leaf folder incidence in paddy crop and in improving the reproductive phase of the crop (with higher productive tillers) and finally in increasing the production of paddy grain yield at reasonable lower doses of the products in the present ternary combination. Thus, the present invention will be cost effective to control yellow stem borer and leaf folder in paddy crop and safer to the environment.

From the above investigations, 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.

Although this invention has been disclosed in the context of certain preferred embodiments and examples, it will be understood by those skilled in the art that the present invention extends beyond the specifically disclosed embodiments to other alternative embodiments and/or uses of the invention and obvious modifications and equivalents thereof. Thus, from the foregoing description, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

We Claim:

[**CLAIM 1**] A synergistic granular insecticidal composition comprising:

a) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives;
b) Emamectin or its agrochemically acceptable salts, esters and derivatives;
c) Fipronil or its agrochemically acceptable salts, esters and derivatives;

[**CLAIM 2**] The synergistic granular insecticidal composition as claimed in claim 1, wherein, composition comprises:

a) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition
b) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition
c) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition.

[**CLAIM 3**] The synergistic granular insecticidal composition as claimed in claim 1, wherein, composition comprises:

a) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present as 0.45% by weight of the composition
b) Emamectin or its agrochemically acceptable salts, esters and derivatives, present as 0.18% by weight of the composition
c) Fipronil or its agrochemically acceptable salts, esters and derivatives, present as of 0.5% by weight of the composition

[**CLAIM 4**] The synergistic granular insecticidal composition as claimed in claim 1, wherein anthranilic diamide insecticide is selected from Cyantraniliprole, Tetraniliprole, Cyclaniliprole, Tetrachlorantraniliprole and Chlorantraniliprole.

[**CLAIM 5**] The synergistic granular insecticidal composition as claimed in claim 1 to 4, which further comprises one or more agrochemically acceptable excipients.

[**CLAIM 6**] The synergistic composition as claimed in claim 1 to 4, wherein the agrochemically acceptable excipients are selected from the group comprising surfactant/dispersing agent, wetting agent, emulsifiers, carriers, fillers, binders, co-binders, curing agent, anti-freezing agent, anti-foaming agent, adjuvants, sticking agent, adjuvants, suspension aid, quick coating agent, anticaking agent, buffering agent, spreader, thickener/thickening agent, antimicrobial/anti-bacterial agent, thickening agent, stabilizers, colouring agents, dyes and solvent or mixtures thereof.

[**CLAIM 7**] The synergistic composition as claimed in claim 6 wherein the dispersing agent is selected form the group comprising Calcium lignosulphonate, Alkyl aryl ether phosphate, tristyryl phenol ethoxylated Acrylic Copolymer/ Ethoxylated Tristryl phenol Sulphate, Naphthalene sulfonic acid, sodium salt condensate with formaldehyde, Ethoxylated oleyl cetyl alcohol, Alkyl aryl sulfonate, Polyalkelene glycol ether, Ethoxylated Fatty alcohol or mixtures thereof and is present in the range of 0.5-10% by weight of the composition.

[**CLAIM 8**] The synergistic composition as claimed in claim 6 wherein the wetting agent is selected from the group comprising Tristyrylphenol ethoxylate, nonionic emulsifier/ Mixture of non-ionic surfactants & Alkoxylated Alcohol/Block copolymer sodium lauryl sulphate, sodium dioctylsulphosuccinate, alkyl phenol ethoxylates; and aliphatic alcohol ethoxylates or mixtures thereof and is present in the range of 0.5-10% by weight of the composition.

[**CLAIM 9**] The synergistic composition as claimed in claim 6, wherein the emulsifiers are selected from the group comprising calcium alkyl benzene sulfonate, calcium hydroxyapatite, Potassium Dihydrogen Phosphate, Sodium Hydroxide, carbonated apatite, calcium carbonate, sodium bicarbonate, tricalcium phosphate, calcium phosphates, carbonated calcium phosphates, amine monomers, lactate dehydrogenase and magnesium hydroxide, Castor oil ethoxylates, modified naphthalene sulphonic acid condensate sodium salt, Acrylate copolymer, polyalkoxylated butyl ether, phenyl naphthalene sulphonates, ethoxylated alkyl phenols, ethoxylated fatty acids, alkoxylated linear alcohols, glyceryl esters, maleic anhydride co-polymers, condensation product of aryl sulphonic acids, addition product of ethylene oxide and fatty acid esters, lignin derivatives, naphthalene formaldehyde condensates, sodium salts of isodecylsulfosuccinic acid half ester, Blend of modified poly ethanoxy ether and sulphated anionic surfactant, blend of alcohol alkoxylates & methyl methacrylate polymer, blend of di

alkyl ate naphthalene sulphonic acid sodium salt, sodium alkyl benesulfonates, sodium salts of sulfonates naphthalene, ammonium salts of Sulfonated naphthalene, salts of poly acrylic acids, salts of phenol Sulfonic acid and salts of naphthalene Sulfonic acids, Ionic and Anionic salts of emulsifiers and mixtures thereof and is present in the range of 0.1-10% by weight of the total composition .

[**CLAIM 10**] The synergistic composition as claimed in claim 6, wherein the binders and co-binders are selected from the group comprising poly-ethylene wax, poly vinyl alcohol, polyesters, polyamides, poly- carbonates, polyurea and polyurethanes, acrylate polymers and copolymers, styrene copolymers, butadiene copolymers, polsaccharides such as starch and cellulose derivatives, polymer of vinyl alcohol, vinyl acetate and vinyl pyrrolidone polymers and copolymers, polyethers, epoxy, phenolic and melamine resins, polyolefins and define copolymers , acrylate polymers such as poly(methacrylate), poly (ethyl methacrylate), poly (methyl methacrylate), acrylate copoylmers and styrene-acrylic copolymers or mixtures thereof and is present in the range of 0.1-10% by weight of the total composition.

[**CLAIM 11**] The synergistic composition as claimed in claim 6, wherein curing agent are selected from the group comprising modified starches, polyacrylates, sodium polyacrylate, polyvinyl alcohol and polyethylene oxide or mixtures thereof and is present in the range of 0.1-10% by weight of the total composition.

[**CLAIM 12**] The synergistic composition as claimed in claim 6 wherein the anti-freezing agent is selected from the group comprising Glycol, Propylene Glycol, Mono ethylene glycol, Glycerin, Diethylene glycol and is present in the range of 0.1-20% by weight of the composition.

[**CLAIM 13**] The synergistic composition as claimed in claim 6, wherein the anti-foaming agent is selected from the group comprising Siloxane polyalkylene oxide, silicone oil, silicone compound, C10～C20 saturated fat acid compounds or C8～C10 aliphatic alcohols compound, silicone antifoam emulsion, dimethylsiloxane, polydimethyl siloxane emulsion, vegetable oil based antifoam, tallow based fatty acids, polyalkyleneoxide modified polydimethylsiloxane and mixtures thereof and is present in the range of 0.01-3% by weight of the composition.

[**CLAIM 14**] The synergistic composition as claimed in claim 6, wherein the adjuvants are selected from the group comprising Silicone Ethoxylated Oil, Polyvinyl Pyrrolidone, Poly vinyl

Alcohol, Blend of poly terpene resin, Polyethylene Wax and is present in the range of 0.1-10% by weight of the composition.

[**CLAIM 15**] The synergistic composition as claimed in claim 6, wherein the carriers and/or fillers are selected from the group comprising talcum powder clays, natural or synthetic silicates, silica, resins, waxes, solid fertilizers, sand, silicon Dioxide, China –Clay, kaolin, talc, starch or mixtures thereof and is present in the range of 0.1-90% by weight of the composition.

[**CLAIM 16**] The synergistic composition as claimed in claim 6 wherein the antimicrobial/anti-bacterial agent are selected from the group comprising Benzisothiazolin-3-one, Formaldehyde, Sodium benzoate, Sodium o-phenyl phenate, 5-chloro-2-methyl-4-isothiazolin-3-one & 2-methyl-4-isothiazolin-3-one,Potassium sorbate or mixtures thereof and is present in the range of 0.01-1% by weight of the composition.

[**CLAIM 17**] The synergistic composition as claimed in claim 6 wherein the thickening agents or thickeners are selected from the group comprising Polysaccharides, carboxymethyl cellulose, bentonite, clay, aluminum magnesium silicate, hydroxy propyl cellulose or mixtures thereof and is present in the range of 0.01-5% by weight of the composition.

[**CLAIM 18**] The synergistic composition as claimed in claim 6 wherein the stabilizers are selected from the group comprising Epoxidised Vegetable Oil and is present in the range of 0.1-10 % by weight of the composition.

[**CLAIM 19**] The synergistic composition as claimed in claim 6 wherein the colouring pigments, dyes are present in the range 0.1-10 % by weight of the composition.

[**CLAIM 20**] The synergistic composition as claimed in claim 6 wherein the solvents are selected from the group comprising heavy aromatic hydrocarbon, N methyl pyrollidone, Di methyl sulfoxide, N- alcohol, Alkyl amide, Vegetable Oil, Mineral Oil, aromatic Solvents, water or mixtures thereof and is present in the range of 0.1-90% by weight of the composition.

[**CLAIM 21**] A synergistic Controlled Release granular insecticidal composition comprising:

a) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives;
b) Emamectin or its agrochemically acceptable salts, esters and derivatives;

c) Fipronil or its agrochemically acceptable salts, esters and derivatives;

[**CLAIM 22**] The synergistic Controlled Release granular insecticidal as claimed in claim 21 comprising:

a) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition
b) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition
c) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition.

[**CLAIM 23**] A synergistic Controlled Release granular insecticidal composition comprising:

a) at least one anthranilic diamide insecticide or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition
b) Emamectin or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition
c) Fipronil or its agrochemically acceptable salts, esters and derivatives, present in the range of 0.01-1% by weight of the composition
d) Micronutrients**,** present in the range of 0.01 to 20 %, by weight of the composition.

[**CLAIM 24**] The synergistic Controlled Release granular insecticidal composition as claimed in claim 23, wherein micronutrient is selected from (zinc sulphate heptahydrate, ZnSO47H2O, zinc sulphate mono hydrate ZnSO4.H2O, chelated zinc as Zn-EDTA, zinc oxide, Zinc Lactate Gluconate, Zinc Polyflavonoid)

[**CLAIM 25**] The synergistic Controlled Release granular insecticidal composition as claimed in claim 21 to 24, wherein anthranilic diamide insecticide is selected from Cyantraniliprole, Tetraniliprole, Cyclaniliprole, Tetrachlorantraniliprole and Chlorantraniliprole.

[**CLAIM 26**] The synergistic Controlled Release granular insecticidal composition as claimed in claim 21 to 25, which further comprises one or more agrochemically acceptable excipients.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2024/053221

A. CLASSIFICATION OF SUBJECT MATTER
A01N43/40,A01N31/14,A01N25/12,A01N43/56 Version=2024.01

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 database consulted during the international search (name of database and, where practicable, search terms used)

PatSeer, 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.
Y	US 20230053477 A1 (ADAMA MAKHTESHIM LTD) 23 FEB 2023 (23-02-2023) see claim-1-29, abstract, para-0012, 0014, 0048,0116, 0118, 0101, 0107	1-26
Y	WO 2022009224 A1 (RAJDHANI PETROCHEMICALS PRIVATE LTD) 13 JAN 2022 (13-01-2022) see claims 1-17, abstract, para-0021-0024, para-0048-0061	1-26

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

Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Citation	Pub.Date	Family	Pub.Date
US 2023053477 A1	23-02-2023	EP 4084616 A1	09-11-2022
		CN 114901074 A	12-08-2022
		BR 112022012971 A2	13-09-2022
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