



(51) International Patent Classification:

A01N 47/22 (2006.01) A01N 47/18 (2006.01)
A01N 37/24 (2006.01)

(21) International Application Number:

PCT/IB2015/059438

(22) International Filing Date:

8 December 2015 (08.12.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

3589/DEL/2014 8 December 2014 (08.12.2014) IN

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.1 7(H))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.1 7(in))
- of inventorship (Rule 4.1 7(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: A NOVEL SYNERGISTIC ENCAPSULATED GRANULAR COMPOSITION

(57) Abstract: The invention discloses a novel synergistic encapsulated granular (CG) composition comprising pyrazole, pyrrole or phenylimidazole insecticide and cartap hydrochloride, and a process for preparing the same.



A NOVEL SYNERGISTIC ENCAPSULATED GRANULAR COMPOSITION

FIELD OF INVENTION

The present invention relates to insecticidal encapsulated granular composition comprising fipronil and cartap hydrochloride, and a method for preparing such composition.

BACKGROUND OF THE INVENTION

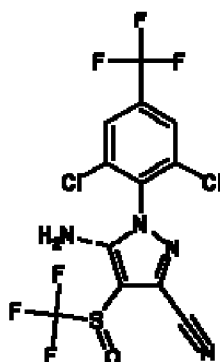
Crop protection technology which includes all pesticides, herbicides, insecticides, fungicide, as well as biotechnological products helps control the thousands of weed species, harmful insects and numerous plant diseases that afflict crops. In the absence of these important crop protection and pest control technologies, food production would decline, many fruits and vegetables would be in short supply and the price of food would rise. Additionally, the production of important fibres for clothing such as cotton would decrease as farmers would lose their harvest and livelihoods to crop pests and diseases. Thus, crop protection is very important to increase the production of agricultural products and at the same time reduce their cost.

Several insecticidal agents and compositions have been developed to control insect pests such as agro-horticultural pests or hygienic pests and in practice have been used as a single or a mixed agent but economically efficient and ecologically safe insect control compositions are still being sought. Insecticidal compositions which allow for reduced effective dosage rates, increased environmental safety and lower the incidence of insect resistance are highly desirable. The rotational application of insect control agents having different modes of action may be adopted for good pest management practice. However, this does not necessarily give satisfactory insect control.

The use of insecticidal combinations is a widespread and documented practice in the agricultural community. Insecticidal combinations offer significant advantages

over individual applications including improved and extended insect control, reduced insecticide rates and application costs, shorter contact times for improved results, less stringent use restrictions, improved selectivity, improved spectrum of insect-pest controlled, reduced cost and reduced residue problems. However, identifying appropriate insecticidal application rates and combinations is essential to achieve synergistic insect control. In view of the above, obtaining an insecticidal combination which demonstrates no cross-resistance to the existing insecticidal agents, no toxicity problems and little negative impact on the environment is extremely difficult. Thus, it is an objective of this invention to provide a synergistic insecticidal combination which demonstrate a high controlling effect along with reduced crop protection cost and reduced environmental load.

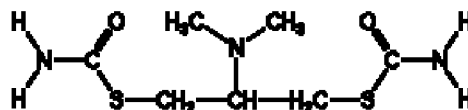
Insecticides with a pyrazole, pyrrole or phenylimidazole group include those described in the applications for European Patents EP 0295117, EP 0460940 or EP 0484165, respectively. Among them is phenyl pyrazole, whose common name is fipronil, and IUPAC name is $(\pm)$ -5-amino-1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-4-(trifluoromethylsulfonyl)pyrazole-3-carbonitrile. Apart from its disclosure in the application EP 02951 17, the properties of the compound fipronil have been published in the report of the 1992 Brighton Crop Protection Conference (Pests and Diseases, pages 29-34). The structure of fipronil is as follows:



Fipronil is a broad-spectrum phenylpyrazole insecticide used to control ants, beetles, cockroaches, fleas, ticks, termites, mole crickets, thrips, rootworms,

weevils and other insects. Fipronil blocks GABAA-gated chloride channels in the central nervous system. Disruption of the GABAA receptors by fipronil prevents the uptake of chloride ions resulting in excess neuronal stimulation and death of the target insect. Insects resistant to pyrethroid, cyclodiene, organophosphorous and/or carbamate insecticides are susceptible to fipronil. Fipronil is broad spectrum insecticide toxic by contact and ingestion.

Cartap hydrochloride (IUPAC S,S'-(2-dimethylaminotrimethylene) bis(thiocarbamate) hydrochloride), a derivative of nereistoxin, a naturally occurring insecticidal substance isolated from the marine segmented worms *Lumbrinereis heteropoda* and *Lumbrinereis brevicirra*. Cartap hydrochloride is a highly effective, broad-spectrum, low toxic and low residual insecticide, causing paralysis by cholinergic blocking action on the central nervous system of insect. It is a systemic insecticide with stomach and contact action. Insects discontinue feeding, and die of starvation. The structure of cartap hydrochloride is as follows:



HCl

Cartap hydrochloride is used against a relatively broad spectrum of insects, e.g., Lepidoptera, Coleoptera, Diptera and Hemiptera. It is especially effective against Lepidoptera such as the rice stem borer, diamond-back moth and common cabbage worm, and Coleoptera such as the Colorado potato beetle, Mexican bean beetle etc. Approximately 70% of the world production of cartap hydrochloride is applied to rice and 30% to other crops, vegetables, potatoes, fruit, tea, etc. Cartap hydrochloride is also used for controlling the rice white-tip nematode by soaking rice seed in an aqueous solution of the insecticide.

Cartap hydrochloride is used against a relatively broad spectrum of insects, e.g., Lepidoptera, Coleoptera, Diptera and Hemiptera. It is especially effective against Lepidoptera such as the rice stem borer, diamond-back moth and common

cabbage worm, and Coleoptera such as the Colorado potato beetle, Mexican bean beetle etc.

The standard composition of cartap hydrochloride available in the art is 50 percent soluble powder and 4 percent granules. However, there are many disadvantages associated with the use of these. For example, disadvantages associated with powder composition and immediate release of active in case of granules resulting in reduced control period.

JP 2001081003 discloses a microbial insecticidal composition containing Cartap hydrochloride (as an active ingredient) along with at least one kind of phenyl alkanic acid amide derivative for paddy field.

JP 09124406 discloses a granulated water dispersible powder containing cartap hydrochloride, alongwith Acephate, Nitenpyram, Bensultap in combination with zinc oxide, MgO, TiO₂, Al₂O₃. JP 08225404, discloses a stabilized agrochemical preparation of cartap hydrochloride and cyclodextrins.

JP 02174702 discloses an active agrochemical composition of cartap hydrochloride mixed with octyldiphenyl phosphate.

WO 2012101659 A1 discloses an active agrochemical composition of fipronil mixed with sulphur.

U.S. Pat. No. 5747519 (A) teaches a termite control composition for soil treatment containing bifenthrin and fipronil, and a method of controlling termites using said composition. However, the publication does not disclose whether a mixture of bifenthrin and fipronil will be suitable in agricultural pest control.

US 2011/0039907 teaches a method of ant control using mixtures of fipronil and a pyrethroid insecticide such as bifenthrin particularly in yards, gardens, parks, lawns and golf courses.

None of the compounds per se or the formulations have been effective in the treatment of rice plants affected by leaf folder and stem borer. There is a need for a formulation that can effectively control leaf folder and stem borer, particularly

leaf folder and stem borer resistant to individual chemical compounds or existing formulations.

There is also a need for insecticidal compositions that offer a broad spectrum of protection, addresses the concerns of resistance, improves foliage, improves handling, improves rainfastness and in various instances, improves crop yield and grain quality. In certain cases, the compositions can be applied as a foliar spray or to the soil, through broadcasting or through drip or trickle irrigation. The latter case of drip or trickle irrigation further optimizes farming practices, which are greatly challenged by an ever-increasing labour and water shortage. In some cases, it has been observed, that the compositions at very low concentrations of the active ingredients can be effectively applied, thereby reducing the burden on the environment. In certain cases, it has also been noted that the compositions at lower rates of the active ingredients in combination together provided a longer duration of control of the pest and avoided pest outbreak and resurgence.

The encapsulated granular (CG) formulations offer significant advantages over the liquid formulations such as ease of handling, ease of use, reduced work exposure, reduced toxicity, reduced spillage and waste disposal and less field drift. Moreover, due to its property of slow release of actives it increases the control period and thereby reducing the environmental load due to repeated sprays.

However, the selection of the appropriate carriers for a encapsulated granular (CG) formulation in order to retain the desired characteristics of the granules such as the liquid holding capacity, non-existent dust levels, high attrition resistance and chemical inertness is not reasonably predictable by a skilled formulator.

SUMMARY OF THE INVENTION

According to an embodiment of the present invention, there is provided an insecticidal composition comprising fipronil and cartap hydrochloride in a synergistic ratio of 1:15-1:8 for efficacious insect control.

According to another embodiment of the present invention, fipronil may be present in an amount in the range from 0.1 to 10% w/w.

According to another embodiment of the present invention, cartap hydrochloride may be present in the range from 1.0 to 25% w/w.

According to another embodiment, the synergistic insecticidal combination may be formulated as dust, powder, granules, encapsulated granules, pellets, tablets, dry flowable, wettable powder and water dispersible granules.

According to another embodiment of the present invention, preferred formulation for the synergistic insecticidal combination is encapsulated granules (CG).

According to another embodiment of the present invention, the synergistic insecticidal composition further comprises a plurality of different ingredients, such as surfactants, binders, stabilizers and carriers to form an encapsulated granular formulation.

In accordance with an embodiment of the invention, there is provided a process for the preparation of a synergistic insecticidal composition, comprising the steps of: (a) admixing Fipronil, Cartap Hydrochloride, surfactants, and stabilizers in a mixing vessel to form a first mixture; (b) homogenizing the first mixture to form a powder; (c) Admixing the powder, a carrier and a binder to form encapsulated granules.

In accordance with an embodiment of the invention, there is provided a method for controlling insects at a locus, comprising treating the locus with synergistic insecticidal composition comprising fipronil and cartap hydrochloride.

In accordance with an embodiment of the invention, there is provided a method for controlling insects, wherein said method increases vigor and yield of crops.

The synergistic insecticidal combination of the present invention is found to be useful in protecting a wide range of crops like fruits, vegetables, cereals etc. against major tissue-chewing, cutting, boring insects of plants from the insect

Orders Orthoptera, Isoptera, Lepidoptera, Coleoptera, Hymenoptera, and Diptera etc.

DETAILED DESCRIPTION OF THE INVENTION

The invention according to its various aspects is particularly pointed out and distinctly claimed in the appended claims read in view of this specification and appropriate equivalents.

It is to be noted, as used in the specification and the appended claims, the singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a mixture of two or more compounds. It should also be noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise. The expression of various quantities in the terms of "% w/w" means the percentage by weight, relative to the weight of the total composition unless otherwise specified.

As used herein CG formulation, WDG formulation, WP formulation, SC formulation are the international denominations adopted by the FAO (Food and Agriculture Organization of the United Nations) to designate encapsulated granules, water dispersible granules, wettable powder and suspension concentrate, respectively.

Many newer and conventional molecules are used for pest management in rice, but the indiscriminate use of these chemicals resulted in reduced percent control due to build-up of the resistance in targeted pest population. There are many reports on resistance of different insects for different molecules. Accordingly, there is provided a novel synergistic insecticidal composition comprising fipronil, and cartap hydrochloride in a synergistic composition for the treatment of wide range of crops like fruited, vegetables, cereals etc. against major tissue-chewing, cutting, boring insects of plants from the insect Orders Orthoptera, Isoptera, Lepidoptera, Coleoptera, Hymenoptera, and Diptera etc. There is provided a

synergistic composition, wherein fipronil may be present in an amount of 0.1-10% w/w and more preferably in an amount of 0.5% w/w. There is also provided a synergistic insecticide composition, wherein cartap hydrochloride may be present in an amount of 1.0-25% w/w and preferably in an amount of 4.0% w/w. The proportion of fipronil to cartap hydrochloride in the synergistic insecticidal composition in terms of mass is 1:15 to 1:8.

The synergistic insecticidal composition of present invention further comprises surfactants, stabilizers, binders and carriers. There is provided a synergistic insecticidal composition, wherein the surfactant is Isopropyl acid phosphate and may be present preferably in an amount of 0.5-1.2% w/w and more preferably in an amount of 0.8% w/w.

The active compounds, present in the synergistic composition are prone to degradation on exposure to high temperatures and oxidation on exposure to atmosphere. Under such conditions, unprotected storage, or storage for very long periods of time can easily result in the synergistic insecticidal composition losing its efficacy or becoming altogether unusable. Accordingly, the synergistic insecticidal composition of the present invention contains a stabilizer in order to protect the active compounds from thermal degradation and oxidation on storage. Alkylphenol ethylene oxide is selected for use as stabilizer in the synergistic insecticidal combination and may be present preferably in an amount of 1.5-1.7% w/w and more preferable 1.7% w/w.

The synergistic insecticidal composition of the present invention also contains china clay as binder to bind the active ingredients to the carrier. The carrier contemplated for the present investigation is preferably river sand.

The synergistic insecticidal composition comprising fipronil and cartap hydrochloride was formulated as encapsulated granules (CG). All the raw materials were verified for conformance to the laid out individual specification. The required quantities of raw materials were weighed, transferred through auto batching system into an agitating vessel and mixed for one hour. The quality of

in-process sample was checked for conformance to the specification. The quality approved in-process sample was transferred to the holding vessel for packaging as per requirement.

The present invention is more particularly described in the following examples that are intended as illustrations only, since numerous modifications and variations within the scope of the present invention will be apparent to those of skill in the art. Unless otherwise noted, all parts, percentages, and ratios reported in the following examples are on a weight basis and all reagent used in the example were obtained or are available from the chemical suppliers.

EXAMPLES

The following examples illustrate embodiments of the proposed invention that are presently best known. However, other embodiments can be practiced that are also within the scope of the present invention.

Example 1-2:

Synergistic insecticidal composition of Fipronil and Cartap hydrochloride

The unit of each value below is "% w/w" i.e., percentage weight by weight, relative to the weight of the composition unless otherwise specified. The compositions tabulated in each of the example 1 - 2 that are tabulated in Table 1 are formulated as encapsulated granule (CG).

Table 1: Examples of synergistic insecticidal composition of Fipronil and Cartap hydrochloride

Component	Function	Examples (% w/w)	
		1	2
Cartap Hydrochloride	A.I.	4.00	3.00

Technical			
Fipronil Technical	A.I.	0.50	0.20
Isopropyl acid phosphate	Surfactant	0.8	0.8
Alkylphenol ethylene oxide	Stabilizer	1.7	1.7
China clay	Binder	7.5	7.35
River sand	Carrier	q.s.	q.s.

A.I.= Active Ingredient

q.s.= quantity Sufficient

Example 3

Process of Manufacturing of Synergistic Insecticidal Composition of Fipronil and Cartap Hydrochloride:

The required amounts of Fipronil and Cartap Hydrochloride (Table 2) are blended with isopropyl acid phosphate and alkylphenol ethylene oxide (NP 85), and blended for one hour. The mixture is homogenized using colloid mill and sieved to remove coarse particles. The river sand (carrier) is added to the mixture and further blended for one hour. China clay is further added to the mixture as binder and further blended for another half hour. Subsequently, the encapsulated granules are tested for quality control.

Table 2: Quantities of technical and raw materials charged

Component	Function	Quantities of raw material charged (Kg/100 kg batch)	
		1 batch	2 batch
Cartap Hydrochloride	A.I.	4.33	3.27
Technical			
Fipronil Technical	A.I.	0.54	0.22

Isopropyl acid phosphate	Surfactant	0.8	0.8
Alkylphenol ethylene oxide	Stabilizer	1.7	1.7
China clay	Binder	7.5	7.35
River sand	Carrier	85.13	86.66

Example 4

Evaluation of the synergistic insecticidal effect of Fipronil and Cartap hydrochloride

Field tests of the compositions according to the present invention were conducted at various controlled trial sites. The performance of the insecticidal composition according to the present invention (Fipronil 0.5% and Cartap Hydrochloride 4% CG) was compared against the known compositions of Fipronil 0.3% G; Cartap Hydrochloride 4.0% G, which were evaluated against leaf folder (*Cnaphalocrosis medinalis*) and stem borer (*Scirpophaga incertulas*) in paddy and also the vigor/yield of the crop was tested. The paddy crop was transplanted in field and harvested after 116 days. Application was made using broadcasting method. Experimental design was in randomized blocks with four replication and each plot measured an area of 100 sq. m. (10 x 10 m). The number of freshly folded leaves and dead hearts/white ear heads was assessed at 15 days after application (DAA).

Table 3 below summarizes the synergistic effect that exists between. fipronil and cartap hydrochloride against leaf folder and stem borer at different concentrations.

In the field of agriculture, it is often understood that the term "synergy" is as defined by Colby S. R. in an article entitled "Calculation of the synergistic and antagonistic responses of herbicide combinations" published in the journal Weeds, 1967, 15, 20-22. The action expected for a given combination of two active components can be calculated as follows:

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

Where,

E = Expected percentage of insecticidal control for the combination for the combination of the two insecticides at defined doses (for example equal to x and y respectively),

$X = X$ is the percentage of insecticidal control observed by the compound (I) at a defined dose (equal to x),

$Y = Y$ is the percentage of insecticidal control observed by the compound (II) at a defined dose (equal to y),

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

Table 3: Synergistic impact of separate and combined treatments for insect pests at different concentrations of synergistic insecticidal composition of Fipronil and cartap hydrochloride CG

Compound		A.I./ha	% control at 15 DAA*	Expected Control (E_t)	Colby's Ratio (E_{a+b}/E_t)
Fipronil		50	$E_a = 40.31$	-	-
Cartap Hydrochloride		750	$E_b = 50.09$	-	-
Fipronil + Hydrochloride	Cartap	50 + 750	$E_{a+b} =$ 79.07	70.21	1.126
Fipronil		60	$E_a = 42.80$	-	-
Cartap Hydrochloride		900	$E_b = 67.71$	-	-
Fipronil +	Cartap	60 + 900	$E_{a+b} =$	81.53	0.995

Compound		A.I./ha	% control at 15 DAA*	Expected Control (E _t)	Colby's Ratio (E _{a+b} /E _t)
Hydrochloride			81.13		
Fipronil		75	E _a = 46.93	-	-
Cartap Hydrochloride		600	E _b = 46.89	-	-
Fipronil + Cartap Hydrochloride		75 + 600	E _{a+b} = 89.7	71.81	1.249
Fipronil		100	E _a = 54.65	-	-
Cartap Hydrochloride		800	E _b = 58.28	-	-
Fipronil + Cartap Hydrochloride		100 + 800	E _{a+b} = 90.49	81.08	1.116

DAA = Days after application

E_a = % control after 15 DAA for Fipronil

E_b = % control after 15 DAA for Cartap Hydrochloride

E_{a+b} = % control after 15 DAA for composition of Fipronil and Cartap Hydrochloride

E_t = Expected % control after 15 DAA for Fipronil and Cartap Hydrochloride

It can be seen from the data presented in Table 3, combination of Fipronil and Cartap hydrochloride demonstrate synergistic effect against insect population.

Example 5: Bio-efficacy of new insecticide against leaf folder and stem borer in paddy crop

Field tests of the compositions according to the present invention were conducted at various trial sites. The performance of the insecticidal composition according to the present invention (Fipronil + Cartap Hydrochloride) was compared against the known compositions of Fipronil 0.3%; Cartap Hydrochloride 4%; and Chlorantraniliprole 0.4% which were evaluated against leaf folder and stem borer in paddy and also the vigor/yield of the crop was tested.

The paddy crop was transplanted in and harvested after 116 days. Application was made using broadcasting method. Experimental design was in randomized blocks with four replications and each plot measured an area of 100 sq. m. (10 x 10 m). The formulations tested were weighed according to doses and mixed in sand and applied using broadcasting method and evaluated for leaf folder and stem borer control in paddy. The reported results were mean of four replications of each evaluation designed in randomized complete blocks. The number of freshly folded leaves (caused by leaf folder) and dead hearts/white ear heads (caused by stem borer) was assessed at 5 DAA (days after application), 10 DAA and 15 DAA. Dead Heart (DH) and White Ear Head (WEH) as used to measure the effects of stem borer. Since the insect bores into the stem and cannot be counted therefore its effect is measured with dead heart/white ear heads.

Details of Experiment

Target Pests: Leaf folder (*Cnaphalocrosis medinalis*) and Stem borer (*Scirpophaga incertulas*)

Crop: Paddy

Application Method: Broad Casting Method

The treatment details are tabulated in Table 4 below.

Table 4: Treatment details for evaluation of Bio-efficacy of new insecticide against leaf folder (*Cnaphalocrosis medinalis*) and stem borer (*Scirpophaga incertulas*) in Paddy

Particular	Treatment	Dose /Acre
T _i	Fipronil 0.5% + Cartap Hydrochloride 4% CG	6 kg
T ₂	Fipronil 0.5% + Cartap Hydrochloride 4% CG	8 kg
T ₃	Chlorantraniliprole 0.4% Granule	4 kg
T ₄	Fipronil 0.3% Granule	10 kg
T ₅	Fipronil 0.2% + Cartap Hydrochloride 3% CG	10 kg
T ₆	Fipronil 0.2% + Cartap Hydrochloride 3% CG	12 kg
T ₇	Cartap Hydrochloride 4% Granule	10 kg
T ₈	Control (No Treatment)	Sand

The bio-efficacy effect of different treatment schedules on paddy crop and the treatment wise yield data of paddy crop is summarized in Table 5-6 below.

Table 5: The bio-efficacy effect of different treatment schedules against leaf folder and stem borer on paddy crop.

Treatment	Dose/ Acre	5 DAA			10 DAA			15 DAA		
		Leaf folder* Damaged leaves after spray (mean of three observations)	Stem borer**		Leaf folder* Damaged leaves after spray (mean of three observations)	Stem borer**		Leaf folder* Damaged leaves after spray (mean of three observations)	Stem borer**	
			Per cent Dead Heart (DH) (%) / hill	Per cent White Ear Head (WEH) (% / hill)		Per cent Dead Heart (DH) (%) / hill	Per cent White Ear Head (WEH) (% / hill)		Per cent Dead Heart (DH) (%) / hill	Per cent White Ear Head (WEH) (% / hill)
T ₁	6 kg	3 (1.87)	0.81 (5.16)	1.63 (7.34)	2.65 (1.77)	0.55 (4.25)	1.02 (5.80)	3.56 (2.01)	0.85 (5.29)	1.75 (7.60)
T ₂	8 kg	2.82 (1.82)	0.69 (4.76)	1.31 (6.57)	2.26 (1.66)	0.45 (3.84)	0.75 (4.96)	3.45 (1.99)	0.79 (5.09)	1.42 (6.85)
T ₃	4 kg	3.82 (2.08)	1.48 (6.98)	3.7 (11.09)	3.56 (2.01)	1.79 (7.69)	3.65 (11.01)	4.92 (2.33)	2.25 (8.63)	4.65 (12.45)
T ₄	10 kg	9.32 (3.13)	3.16 (10.23)	8.95 (17.40)	9.8 (3.21)	3.86 (11.33)	9.9 (18.33)	13.35 (3.72)	5.1 (13.05)	12.56 (20.75)
T ₅	10 kg	4.36 (2.21)	1.17 (6.20)	3.86 (1.13)	4.02 (2.13)	1.25 (6.42)	3.99 (11.53)	5.65 (2.48)	1.69 (7.46)	5.35 (13.37)

τ_6	12 kg	4.23 (2.1 7)	1.02 (5.80)	3.47 (10.7 4)	3.85 (2.0 8)	1.05 (5.88)	3.75 (11.1 6)	5.35 (2.4 2)	1.52 (7.08)	4.56 (12.3 3)
τ_7	10 kg	8.75 (3.0 4)	2.93 (9.86)	8.15 (16.5 8)	8.95 (3.0 7)	3.2 (10.3 1)	9.41 (17.8 7)	12.2 5 (3.5 7)	4.75 (12.5 9)	11.65 (19.9 5)
T_8	San d	15.6 7 (4.0 2)	5.8 (13.9 4)	16.59 (24.0 3)	17.8 5 (4.2 8)	7.92 (16.3 5)	20.99 (27.2 6)	23.2 5 (4.8 7)	9.89 (18.3 2)	25.01 (30.0 0)
SE m $\pm$	-	0.00 4	0.05	0.039	0.00 3	0.067	0.143	0.00 4	0.155	0.032
CD @ 5 %	-	0.01 2	0.154	0.118	0.01 1	0.206	0.438	0.01 1	0.051	0.098

SEm $\pm$: Standard Error of Mean; C.D @ 5%: Critical Difference

* Values in Parentheses are $V_{x+0.5}$ transformed value. ** Values in Parentheses are arc sin transformed value

Table 6: Treatment wise yield data of Paddy crop

The sun dried grains obtained after threshing and cleaning from the harvested area of each plot were weighed for recording grain yield in each plot. The grain yield thus obtained was then converted into kg hectare⁻¹ for each plot. Similarly, the straw obtained after recovering grains from the harvested area of each plot was weighed for recording straw yield in each plot. The straw yield thus obtained was then converted into kg hectare⁻¹ for each plot.

Treatment	Dose/Acre	Yield (quintal/hectare)	Straw yield (quintal/hectare)
T ₁	6 kg	45.50	59.21
T ₂	8 kg	46.65	60.12
T ₃	4 kg	45.30	59.96
T ₄	10 kg	37.97	49.85
T ₅	10 kg	41.41	55.25
T ₆	12 kg	43.12	58.19
T ₇	10 kg	39.60	52.45
T ₈	Sand	32.32	45.01
SEm ±	-	1.06	0.93
CD @ 5%	-	3.24	2.85

SEm±: Standard Error of Mean;

CD @ 5%: Critical Difference

The aforementioned trial results indicate that the Fipronil 0.5% + Cartap Hydrochloride 4% encapsulated Granules (CG) composition of present invention is most effective against all the target insects, with almost negligible insect infestation even after 15 DAA and better crop condition i.e. good crop stand, crop height, better crop vigour and growth, increased grain weight/hill. Similar effect was observed with its higher dose and Fipronil 0.2% + Cartap Hydrochloride 3% CG @ 10 kg/Acre and Chlorantraniliprole 0.4% Granule, whereas, Fipronil 0.3% and Cartap Hydrochloride 4% failed to show any effect.

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

Claims:

1. A synergistic insecticidal composition comprising fipronil and cartap hydrochloride in a ratio of 1:15 to 1:8.
2. The synergistic insecticidal composition as claimed in claim 1, wherein fipronil is present in an amount in the range from 0.1-10% w/w.
3. The synergistic insecticidal composition as claimed in claim 1, wherein cartap hydrochloride is present in an amount in the range from 1-25% w/w.
4. The synergistic insecticidal composition as claimed in any of the preceding claims, wherein said composition is formulated as encapsulated granules (CG), water dispersible granules (WDG), wettable powder (WP), soluble powder (SP) or suspension concentrate (SC).
5. The synergistic insecticidal composition as claimed in claim 4, wherein the composition is formulated as encapsulated granules (CG).
6. The synergistic insecticidal composition as claimed in any of the claims 1-5, wherein the composition further comprises a surfactant, a stabilizer, a binder and a carrier to form an encapsulated granular formulation (CG).

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2015/059438

A. CLASSIFICATION OF SUBJECT MATTER

A01N4 7/22, A01N37/24, A01N4 7/18 Version=2 016 .01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N

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

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

IPO INTERNAL DATABASE, PATSEER

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevancy to claim No.
A	WO 2012101659; SHAH DEEPAK PRANJIVANDAS ; 2012 August 02. Claims 1-12	1-6
A	WO 2010095151; SHAH DEEPAK PRANJIVANDAS [NA] ;RAMDAS PUTHENVEETIL KUNJUKRISHNA MENON [IN] ; VADAKKEKUTTU BALACHANDRAN THANKAPPAN [IN] ; 2010 August 26. Claims 1-21	1-6
A	IN 215 6/MUM/ 2006; SUDARSHAN CHEMICAL INDUSTRIES LIMITED; 2008 NOVEMBER 19. Claim- 1	1-6



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

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

"I"

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

"X"

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

"Y"

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

"&"

document member of the same patent family

Date of the actual completion of the international search

18-03-2016

Date of mailing of the international search report

18-03-2016

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT / IB2 015 / 059438

Citation	Pub. Date	Family	Pub. Date
Wo 2012101659 A1	02-08-2012	AE 2015230475 A1	20-08-2015
		RU 2013139708 A	10-03-2015
		EP 2667719 A1	04-12-2013
		AU 2012210144 A1	15-08-2013
Wo 2010095151 A2	26-08-2010	US 2011306502 A1	15-12-2011
		NZ 595277 A	29-11-2013
		CN 105360114 A	02-03-2016
		AU 2010215126 A2	08-09-2011