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(54) Title: A SYNERGISTIC COMPOSITION COMPRISING INSECTICIDES AND FUNGICIDES

(57) Abstract: A composition for treating pest infestations in plants is provided, the composition comprising: (A) an insecticidal component comprising: (A1) fipronil; and (A2) thiodicarb; and (B) a fungicidal component comprising: (B1) azoxystrobin; and (B2) carbendazim. A method of preventing, controlling and/or treating insecticidal, nematode and fungicidal infestations in plants is also provided, the method comprising applying to the plants, their locus and/or plant propagation materials the components: (A) an insecticidal component comprising: (A1) fipronil; and (A2) thiodicarb; and (B) a fungicidal component comprising: (B1) azoxystrobin; and (B2) carbendazim. The composition and the method are particularly suitable for the treatment of maize, rice, wheat, soybean, cotton and sugarcane.



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## **A SYNERGISTIC COMPOSITION COMPRISING INSECTICIDES AND FUNGICIDES**

### **CROSS REFERENCE TO RELATED APPLICATIONS**

5           This application claims the priority of Brazil Patent Application No. BR 10 2019 004065 3, filed on February 27, 2019, and titled with “A SYNERGISTIC COMPOSITION COMPRISING INSECTICIDES AND FUNGICIDES”, and the disclosures of which are hereby incorporated by reference.

### **FIELD**

10           The present invention relates to a synergistic composition comprising (A) an insecticidal component; and (B) a fungicidal component. The present invention is also related to a method to prevent, control and/or treat insect, nematode and fungal infestations in plants, plant parts and/or their surroundings by applying to the plant or locus to be treated the aforementioned insecticidal component (A) and the fungicidal component (B), such as by  
15           way of a synergistic composition according to the present invention. The present invention also relates to the use of the aforementioned components (A) and (B) in the treatment and/or prevention of insect, nematode and fungal infestations in plants or parts thereof, in particular in the treatment of seeds, foliage and soil applications.

### **BACKGROUND**

20           Nematode and insect infestations and fungal diseases represent a major threat to economically important agricultural crops, such as cereals, fibrous plants, leguminous plants and sugarcane. The yield of crop plants, for example, sugarcane and soybean, are adversely impacted by nematode, insect and fungal infestations. Therefore, there is a continuing need  
25           to provide improved techniques for preventing, controlling and/or treating nematode, insect and fungal infestations, thereby increasing the yield of crop plants.

          Researchers in the field of chemistry have synthesized a wide range of compounds and formulations to treat nematode, insect and fungal infestations. Different types and classes of insecticides and fungicides are known in the art and many are available  
30           commercially in the market. In some cases, insecticidal and fungicidal active ingredients have been shown to be more effective in combination than when applied individually. This

effect is known in the art as "synergism." As defined in the Herbicide Handbook of the Weed Science Society of America, Seventh Edition, 1994, page 318, "synergism" [is] an interaction of two or more factors such that the effect when combined is greater than the predicted effect based on the response to each factor applied separately."

## 5 SUMMARY

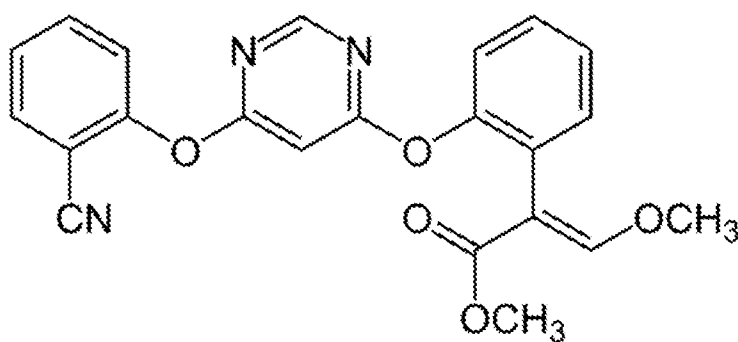
The present invention is based on the surprising discovery that certain fungicides and insecticides display a synergistic effect when applied or employed in combination.

The insecticidal and fungicidal active ingredients employed to provide the synergistic effects of this invention are independently known in the art for their use in plant protection.

10 In particular, the active ingredients employed in the present invention are disclosed in The Pesticides Manual, Twelfth Edition, 2000, published by The British Crop Protection Council. They are also commercially available.

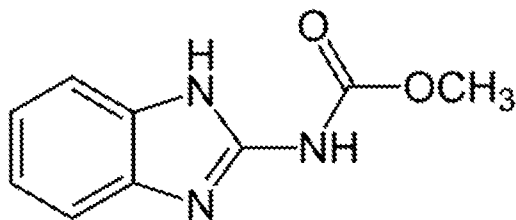
Azoxystrobin (methyl (2E)-2-{2-[6-(2-cyanophenoxy)pyrimidin-4-yloxy]phenyl}-3-methoxyacrylate), a strobilurin-type fungicide, is a well-known fungicide having a broad  
15 spectrum of disease control. It is extracted from the fungus *Strobilurus tenacellus*. Azoxystrobin has a suppressive effect on other fungi, reducing competition for nutrients. Azoxystrobin inhibits electron transfer between cytochrome b and cytochrome C<sub>1</sub> at the ubiquinol oxidising site in mitochondria of the target fungi, disrupting metabolism and preventing growth of the target fungi.

20 Azoxystrobin can be represented by the following formula:



Carbendazim (methyl 1H-benzimidazol-2-ylcarbamate) belongs to the benzimidazole class of compounds and is known in the art. Benzimidazoles are a class of systemic fungicides exhibiting both protective and curative actions. The benzimidazoles are absorbed  
25 through the leaves and roots of the plant, with translocation principally acropetally, and function by inhibition of the beta-tubulin assembly of the target fungi.

Carbendazim can be represented by the following formula:

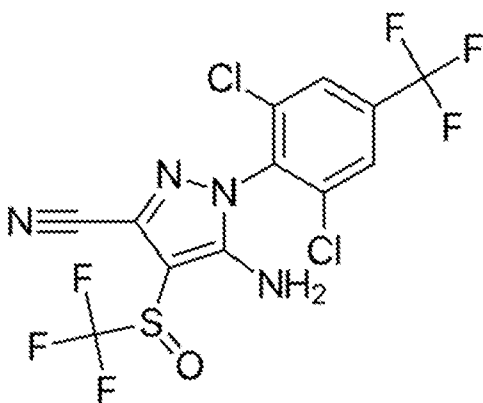


Fipronil

(5-amino-1-(2,6-dichloro- $\alpha,\alpha,\alpha$ -trifluoro-p-tolyl)-4-

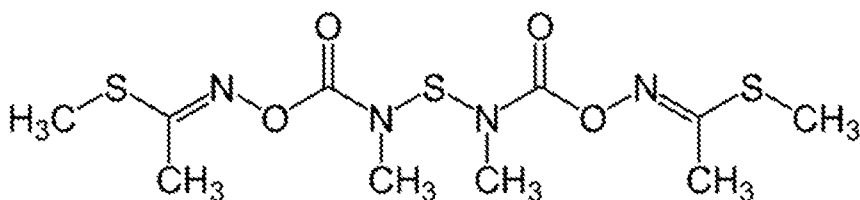
[(trifluoromethyl)sulfinyl]-1H-pyrazole-3-carbonitrile) belongs to a class of insecticides known as the phenylpyrazoles. Fipronil acts on insects to interfere with the passage of chloride ions through the gamma-aminobutyric acid (GABA)-regulated chloride channel, disrupting CNS activity. Fipronil is moderately systemic and can be used to control insects when applied as a soil or seed treatment. A method to prepare Fipronil is disclosed in WO 2013/037291 A1.

Fipronil can be represented by the following formula:



Thiodicarb ((3EZ,12EZ)-3,7,9,13-tetramethyl-5,11-dioxa-2,8,14-trithia-4,7,9,12-tetraazapentadeca-3,12-diene-6,10-dione) is an N-methyl oxyimidothioate carbamate insecticide. Thiodicarb is a neurotoxic compound and its mode of action is via the inhabitation of cholinesterase enzymes in the target insects.

Thiodicarb can be represented by the following formula:



Surprisingly, it has been found that employing a combination of azoxystrobin, carbendazim, fipronil and thiodicarb gives rise to an unexpectedly, synergistic activity in the control of infestations of both insects and fungi.

5           The present invention provides in a first aspect a composition comprising:

(A) an insecticidal component comprising:

(A1) fipronil; and

(A2) thiodicarb;

and

10          (B) a fungicidal component comprising:

(B1) azoxystrobin; and

(B2) carbendazim.

15          In a further aspect, the present invention provides a method of preventing, controlling and/or treating insecticidal, nematode and fungicidal infestations in plants, the method comprising applying to the plants, their locus and/or plant propagation materials the components:

(A) an insecticidal component comprising:

(A1) fipronil; and

20          (A2) thiodicarb;

and

(B) a fungicidal component comprising:

(B1) azoxystrobin; and

(B2) carbendazim.

25

In a still further aspect of the present invention there is provided the use in preventing, controlling and/or treating insecticidal, nematode and fungicidal infestations in plants of the components:

(A) an insecticidal component comprising:

(A1) fipronil; and

(A2) thiodicarb;

and

5 (B) a fungicidal component comprising:

(B1) azoxystrobin; and

(B2) carbendazim.

10 It has now surprisingly been found that when employing a combination of active components comprising (A) an insecticidal component comprising (A1) fipronil and (A2) thiodicarb; and (B) a fungicidal component comprising (B1) azoxystrobin and (B2) carbendazim on the plants, plant parts and/or their surroundings, particularly on cereals, fiber plants, leguminous plants and sugarcane, an excellent performance in preventing, controlling and/or treating insect, nematode and fungal infestations may be observed.

15 The compositions and method of the present invention employ a combination of components (A1), (A2), (B1) and (B2). It has been found that this combination of active components exhibit synergy and can provide advantages over the individual use of the active ingredients of components (A) and (B). In particular, the rates of application of the individual components (A1), (A2), (B1) and (B2) can be markedly reduced while maintaining  
20 a high level of insecticidal or fungicidal efficacy. The combination exhibits a considerably broader spectrum against which it is effective than does any of the components employed alone. Further, the combination can control fungal and/or insect and/or nematode species at a low application rate at which the individual active compounds alone are ineffective. The combination can exhibit a speed of action which is faster than that which would have been  
25 predicted from the speed of action of the individual active compounds.

The composition and method employ an insecticidal effective amount of component (A) and a fungicidal effective amount of component (B).

## DETAILED DESCRIPTION

As used herein:

The term "effective amount" means the quantity of a referenced compound or combination of such compounds that is capable of controlling insect, nematode and/or fungal infestations of plants, in particular preventing, controlling and/or treating insect, nematode and/or fungal infestations of plants.

5 "Plant" as used herein, refers to all plant and plant populations such as desired and undesired wild plants or crop plants.

"Plant parts" as used herein, refers to all parts and organs of plants, such as shoots, leaves, needles, stalks, stems, fruit bodies, fruits, seeds, roots, tubers and rhizomes. Harvested materials, as well as vegetative and generative propagation materials, for example cuttings,  
10 tubers, meristem tissue, rhizomes, offsets, seeds, single and multiple plant cells and any other plant tissues, are also included in the term "plant parts".

"Surrounding" or "locus" refers to the place where the plants are growing, the place where the plant propagation materials of the plants are sown or the place where the plant propagation materials of the plants will be sown.

15

The components (A) and (B) together may be present in the composition in any suitable amount. The total amount of components (A) and (B) may be from 1% by weight, preferably from 2%, more preferably from 5%, still more preferably from 10%, more preferably still from 15%, especially from 20% by weight. The total amount of components  
20 (A) and (B) present in the composition may be up to 95% by weight, preferably up to 90%, more preferably up to 85%, still more preferably up to 80%, more preferably still up to 70% by weight. Components (A) and (B) may be present in an amount of from about 2% to about 95% by weight of the composition, preferably from about 25% to about 80% by weight of the composition, more preferably from about 35% to about 70%, even more preferred from about  
25 45% to about 65% by weight of the composition.

The insecticidal component (A) may be present in the composition of the present invention in any suitable amount. Preferably, component (A) is present in the composition in an amount of from 5% by weight, more preferably from 10%, still more preferably from 15%, more preferably still from 20% by weight of the composition. Component (A) may be  
30 present in the composition in an amount of up to 95% by weight, preferably up to 90%, more preferably up to 85%, still more preferably up to 80%, more preferably still up to 75% by weight. Component (A) may be present in an amount of from about 20% to about 80% by

weight of the composition, preferably from about 30% to about 70% by weight of the composition, more preferably from about 35% to about 60% by weight, still more preferably from about 35% to about 50% by weight of the composition.

5 Fipronil may be present in the composition of the present invention in any suitable amount. Preferably, fipronil is present in the composition in an amount of from 1% by weight, more preferably from 2%, still more preferably from 3%, more preferably still from 5% by weight of the composition. Fipronil may be present in the composition in an amount of up to 30% by weight, preferably up to 25%, more preferably up to 20%, still more preferably up to 15%, more preferably still up to 10% by weight. Fipronil may be present in  
10 an amount of from about 1% to about 20% by weight of the composition, preferably from about 1% to about 15%, more preferably from about 1% to about 10% by weight of the composition, still more preferably from about 5% to about 10% by weight of the composition. In some preferred embodiments, fipronil is present in an amount of from about 7% by weight of the composition.

15 Thiodicarb may be present in the composition of the present invention in any suitable amount. Preferably, thiodicarb is present in the composition in an amount of from 5% by weight, more preferably from 10%, still more preferably from 15%, more preferably still from 20% by weight of the composition. Thiodicarb may be present in the composition in an amount of up to 80% by weight, preferably up to 75%, more preferably up to 70%, still more preferably up to 65%, more preferably still up to 60% by weight. Thiodicarb may be present  
20 in an amount of from about 10% to about 70% by weight of the composition, preferably from about 20% to about 60%, more preferably from about 25% to about 50% by weight of the composition, still more preferably from about 30% to about 40% by weight of the composition. In some preferred embodiments, thiodicarb is present in an amount of from  
25 about 35% by weight of the composition.

The fungicidal component (B) may be present in the composition of the present invention in any suitable amount. Preferably, component (B) is present in the composition in an amount of from 1% by weight, more preferably from 2%, still more preferably from 3%, more preferably still from 5% by weight of the composition. Component (B) may be present  
30 in the composition in an amount of up to 50% by weight, preferably up to 40%, more preferably up to 35%, still more preferably up to 30%, more preferably still up to 25% by weight. Component (B) may be present in an amount of from about 1% to about 30% by weight of the composition, preferably from about 1% to about 20%, more preferably from

about 1% to about 15% by weight of the composition, still more preferably from about 5% to about 10% by weight of the composition.

Azoxystrobin may be present in the composition of the present invention in any suitable amount. Preferably, azoxystrobin is present in the composition in an amount of from 5 0.1% by weight, more preferably from 0.2%, still more preferably from 0.3%, more preferably still from 0.5% by weight of the composition. Azoxystrobin may be present in the composition in an amount of up to 15% by weight, preferably up to 10%, more preferably up to 5%, still more preferably up to 2.5%, more preferably still up to 1% by weight. Azoxystrobin may be present in an amount of from about 0.1% to about 10% by weight of 10 the composition, preferably from about 0.1% to about 5%, more preferably from about 0.1% to about 2.5% by weight of the composition, still more preferably from about 0.1% to about 1% by weight of the composition. In some preferred embodiments, azoxystrobin is present in an amount of from about 0.8% by weight of the composition.

Carbendazim may be present in the composition of the present invention in any 15 suitable amount. Preferably, carbendazim is present in the composition in an amount of from 1% by weight, more preferably from 2%, still more preferably from 3%, more preferably still from 5% by weight of the composition. Carbendazim may be present in the composition in an amount of up to 30% by weight, preferably up to 25%, more preferably up to 20%, still more preferably up to 15%, more preferably still up to 10% by weight. Carbendazim may be 20 present in an amount of from about 1% to about 20% by weight of the composition, preferably from about 1% to about 15%, more preferably from about 1% to about 10% by weight of the composition, still more preferably from about 5% to about 10% by weight of the composition. In some embodiments, carbendazim is present in an amount of from about 7% by weight of the composition.

25 In certain embodiments, the weight percentages of components in the composition are independently: from about 1% to about 10% of fipronil; from about 25% to about 50% of thiodicarb; from about 0.1% to about 2.5% of azoxystrobin; and from about 1% to about 10% of carbendazim by weight of the composition.

In some embodiments, the weight percentages of the components in the composition 30 are independently: from about 5% to about 10% of fipronil; from about 30% to about 40% of thiodicarb; from about 0.1% to about 1% of azoxystrobin by weight of the composition; and from about 5% to about 10% of carbendazim by weight of the composition.

The components (A) and (B) may be present in the composition or employed in any amounts relative to each other necessary to provide the enhanced or synergistic effect of the combination. In particular, the weight ratio of the components (A) and (B) may be in the range of from about 50:1 to about 1:50, preferably from 40:1 to 1:40, more preferably from about 30:1 to 1:30, still more preferably from 25:1 to 1:25, more preferably still from 20:1 to 1:20, especially from about 15:1 to about 1:15, more especially from about 12:1 to about 1:12. A weight ratio of components (A) and (B) of from about 9:1 to about 1:9 is preferred for many embodiments.

It is preferred that component (A) is employed in a greater amount by weight than the amount by weight of component (B). Components (A) and (B) are preferably employed in a weight ratio of from 1.1:1, preferably from 1.2:1, more preferably from 1.3:1, still more preferably from 1.5:1, still more preferably from 2:1, especially from 2.25:1, more especially from 2.5:1. Components (A) and (B) are preferably employed in a weight ratio of up to 50:1, preferably up to 40:1, more preferably up to 30:1, still more preferably up to 25:1, more preferably still up to 20:1, especially up to 15:1, more especially up to 10:1.

In some embodiments, the weight ratio of the components (A) to (B) employed in the present invention is about 9:1, or 8:1 or 7:1 or 6:1 or 5:1 or 4:1 or 3:1 or 2:1 or 1:1. In some embodiments, for example for seed treatment, the weight ratio of the components (A) to (B) employed is about 5:1.

The weight ratio of component (A1) fipronil to component (A2) thiodicarb employed in the present invention may be from 15:1 to 1:15, preferably from 10:1 to 1:10, more preferably from 5:1 to 1:5. It is preferred that thiodicarb is employed in an amount in weight excess to the amount of fipronil. Preferably, the weight ratio of fipronil to thiodicarb is up to 1:15, more preferably up to 1:10, still more preferably up to 1:8, more preferably still up to 1:6. A weight ratio of fipronil to thiodicarb of from 1:2 to 1:8, in particular from 1:3 to 1:7, more particularly from 1:4 to 1:6, even more particularly from 1:4.5 to 1:5.5, especially about 1:5 is preferred for many embodiments.

The weight ratio of component (B1) azoxystrobin to component (B2) carbendazim employed in the present invention may be from 20:1 to 1:20, preferably from 15:1 to 1:15, more preferably from 10:1 to 1:10. It is preferred that carbendazim is employed in an amount in weight excess to the amount of azoxystrobin. Preferably, the weight ratio of azoxystrobin to carbendazim is up to 1:20, more preferably up to 1:15, still more preferably up to 1:12,

more preferably still up to 1:10. A weight ratio of azoxystrobin to carbendazim of from 1:5 to 1:12, in particular from 1:6 to 1:11, more particularly from 1:7 to 1:10, even more particularly from 1:8 to 1:9, especially about 1:8.3 is preferred for many embodiments.

5 In the method of the present invention, the components (A1), (A2), (B1) and (B2) may be employed in a single composition or as separate compositions comprising one or more of the active components. In a preferred embodiment of the invention, the method employs a composition comprising components (A) and (B).

10 The compositions of the present invention and employed in the present invention may comprise the active components in combination with one or more auxiliaries. The auxiliaries employed in the composition will depend upon the type of formulation and/or the manner in which the formulation is to be applied by the end user. Formulations incorporating the composition of the present invention are described hereinafter. Suitable auxiliaries which may be comprised in the composition according to the invention are all customary  
15 formulation adjuvants or components, such as extenders, carriers, solvents, surfactants, stabilizers, anti-foaming agents, anti-freezing agents, preservatives, antioxidants, colorants, thickeners, solid adherents and inert fillers. Such auxiliaries are known in the art and are commercially available. Their use in the formulation of the compositions for use in the present invention will be apparent to the person skilled in the art.

20 The compositions may comprise one or more inert fillers. Such inert fillers are known in the art and available commercially. Suitable fillers in a form of a solid include, for example, natural ground minerals, such as kaolin, alumina, talc, chalk, quartz, attapulgite, montmorillonite, and diatomaceous earth, or synthetic ground minerals, such as highly dispersed silicic acid, aluminum oxide, silicates, and calcium phosphates and calcium hydrogen phosphates. Suitable inert fillers for granules include, for example, crushed and  
25 fractionated natural minerals, such as calcite, marble, pumice, sepiolite, and dolomite, or synthetic granules of inorganic and organic ground materials, as well as granules of organic material, such as sawdust, coconut husks, corn cobs, and tobacco stalks.

30 The compositions may include one or more surfactants. Suitable surfactants include non-ionic, cationic and anionic surfactants. The compositions may employ surfactants or surfactant mixtures which have good emulsifying, dispersing and wetting properties, depending on the nature of the active compound to be formulated. Suitable surfactants are known in the art and are commercially available. Suitable anionic surfactants can be both so-

called water-soluble soaps and water-soluble synthetic surface-active compounds. Soaps which may be used are the alkali metal, alkaline earth metal or substituted or unsubstituted ammonium salts of higher fatty acids (C<sub>10</sub> to C<sub>22</sub>), for example the sodium or potassium salt of oleic or stearic acid, or salts of natural fatty acid mixtures. The surfactant can be an  
5 emulsifier, dispersant or wetting agent of an ionic or non-ionic type. Examples of such surfactants which may be used are salts of polyacrylic acids, salts of lignosulphonic acid, salts of phenylsulphonic or naphthalenesulphonic acids, polycondensates of ethylene oxide with fatty alcohols or with fatty acids or with fatty amines, substituted phenols, especially alkylphenols, sulphosuccinic ester salts, taurine derivatives, especially alkyltaurates, or  
10 phosphoric esters of polyethoxylated phenols or alcohols. The presence of at least one surfactant is generally required when the active compound and/or the inert carrier and/or auxiliary/adjuvant are insoluble in water and the vehicle for the final application of the composition is water.

The compositions may optionally further comprise one or more polymeric stabilizers. Suitable polymeric stabilizers that may be used in the present invention include, but are not  
15 limited to, polypropylene, polyisobutylene, polyisoprene, copolymers of monoolefins and diolefins, polyacrylates, polystyrene, polyvinyl acetate, polyurethanes or polyamides. Suitable stabilizers are known in the art and are commercially available.

The surfactants and polymeric stabilizers mentioned above are generally believed to  
20 impart stability to the composition, in turn allowing the composition to be formulated, stored, transported and applied.

Suitable anti-foaming agents for use in the compositions employed in the present invention include all substances which can normally be used for this purpose in agrochemical compositions. Suitable anti-foaming agents are known in the art and are available  
25 commercially. Particularly preferred anti-foaming agents are mixtures of polydimethylsiloxanes and perfluoroalkylphosphonic acids, such as the silicone anti-foaming agents available from GE or Compton.

Suitable organic solvents that may be included in compositions for use in the present invention are selected from all customary organic solvents which thoroughly dissolve the  
30 active compounds employed. Again, suitable organic solvents for the active components (A1), (A2), (B1) and (B2) are known in the art. The following may be mentioned as being preferred: N-methyl pyrrolidone, N-octyl pyrrolidone, cyclohexyl-1-pyrrolidone; or

SOLVLESSO™<sup>200</sup>, a mixture of paraffinic, isoparaffinic, cycloparaffinic and aromatic hydrocarbons. Suitable solvents are commercially available.

Suitable preservatives for use in the compositions include all substances which can normally be used for this purpose in agrochemical compositions of this type and again are well known in the art. Suitable examples that may be mentioned include PREVENTOL® (from Bayer AG) and PROXEL® (from Bayer AG).

Suitable antioxidants for use in the compositions are all substances which can normally be used for this purpose in agrochemical compositions, as is known in the art. Preference is given to butylated hydroxytoluene, for example.

Suitable thickeners that may be used in the compositions include all substances which can normally be used for this purpose in agrochemical compositions. For example xanthan gum, PVOH, cellulose and its derivatives, clay hydrated silicates, magnesium aluminum silicates or a mixture thereof. Again, such thickeners are known in the art and available commercially.

The compositions may further comprise one or more solid adherents. Such adherents are known in the art and available commercially. They include organic adhesives, including tackifiers, such as celluloses of substituted celluloses, natural and synthetic polymers in the form of powders, granules, or lattices, and inorganic adhesives such as gypsum, silica or cement.

In addition, depending upon the formulation, the compositions according to the invention or employed in the present invention may also comprise water.

The compositions and method of the present invention can be used in the agricultural sector and related fields of use for control insects; nematodes; and fungi, for example, but not limited to:

*Alabama spp., Alternaria spp., Anticarsia spp., Aphis spp., Aracanthus spp., Aspergillus spp., Asperisporium spp., Atta spp., Bemisia spp., Bipolaris spp., Cercospora spp., Cerotelium spp., Colletotrichum spp., Conoderus spp., Cornitermes spp., Corynespora spp., Crysodeixis spp., Deois spp., Diabrotica spp., Diaporthe spp., Dichelops spp., Diloboderus spp., Drechslera spp., Elasmopalpus spp., Elsinoe spp., Empoasca spp., Enneothrips spp., Epinotia spp., Erysiphe spp., Euetheola spp., Eutinobothrus spp., Frankliniella spp., Fusarium spp., Helicoverpa spp., Heliothis spp., Hemileia spp., Heterotermes spp., Julus spp., Lasiodiplodia spp., Leandria spp., Meloidogyne spp.,*

*Metopolophium* spp., *Microsphaera* spp., *Migdolus* spp., *Mycosphaerella* spp.,  
*Neocapritermes* spp., *Oidium* spp., *Oryzophagus* spp., *Penicillium* spp., *Phaeoisariopsis* spp.,  
*Phoma* spp., *Phomopsis* spp., *Phyllophaga* spp., *Phyllosticta* spp., *Plasmopara* spp.,  
*Porcellio* spp., *Pratylenchus* spp., *Procornitermes* spp., *Pseudocercospora* spp.,  
5 *Pseudoperonospora* spp., *Puccinia* spp., *Pyricularia* spp., *Ramularia* spp., *Rhizoctonia* spp.,  
*Rhopalosiphum* spp., *Sclerotinia* spp., *Septoria* spp., *Sphaerotheca* spp., *sphenophorus* spp.,  
*Spodoptera* spp., *Stagonospora* spp., *Sternechus* spp., *Syntermes* spp., *Thrips* spp.,  
*Tranzschelia* spp., *Uromyces* spp.,

Specific species that may be controlled using the present invention include:

10 *Alabama argillacea*, *Alternaria brassicae*, *Alternaria dauci*, *Alternaria porri*, *Alternaria solani*,  
*Anticarsia gemmatilis*, *Aphis gossypii*, *Aracanthus mourei*, *Aspergillus flavus*,  
*Aspergillus* spp., *Asperisporium caricae*, *Atta capiguara*, *Bemisia tabaci*, *Bipolaris sorokiniana*,  
*Cercospora arachidicola*, *Cercospora beticola*, *Cercospora officicola*,  
*Cercospora kikuchii*, *Cercospora sojae*, *Cerotelium fici*, *Colletotrichum gloeosporioides*,  
15 *Colletotrichum gossypii* var., *Colletotrichum lindemuthianum*, *Colletotrichum truncatum*,  
*Conoderus scalaris*, *Cornitermes bequaerti*, *Cornitermes cumulans*, *Corynespora cassiicola*,  
*Crysodeixis includens*, *Deois flavopicta*, *Deois lignosellus*, *Diabrotica speciosa*, *Diaporthe phaseolorum* var.,  
*Dichelops melacanthus*, *Diloboderus abderus*, *Drechslera teres*,  
*Elasmopalpus lignosellus*, *Elsinoe ampelina*, *Elsinoe australis*, *Elsinoe fawcetti*, *Empoasca*  
20 *kraemeri*, *Enneothrips flavens*, *Epinotia aporema*, *Erysiphe diffusa*, *Euetheola humilis*,  
*Eutinobothrus brasiliensis*, *Frankliniella schultzei*, *Frankliniella williamsi*, *Fusarium graminearum*,  
*Fusarium moniliforme*, *Fusarium oxysporum* f.sp., *Fusarium pallidoroseum*,  
*Helicoverpa armigera*, *Heliothis virescens*, *Hemileia vastatrix*, *Heterotermes tenuis*, *Julus hesperus*,  
*Lasiodiplodia theobromae*, *Leandria momordicae*, *Meloidogyne incognita*,  
25 *Meloidogyne javanica*, *Metopolophium dirhodum*, *Microsphaera diffusa*, *Migdolus fryanus*,  
*Mycosphaerella fragariae*, *Mycosphaerella musicola*, *Neocapritermes opacus*, *Oidium* sp.,  
*Oryzophagus oryzae*, *Penicillium* spp., *Phaeoisariopsis griseola*, *Phoma costaricensis*,  
*Phomopsis sojae*, *Phyllophaga cuyabana*, *Phyllophaga triticophaga*, *Phyllosticta citricarpa*,  
*Plasmopara viticola*, *Porcellio laevis*, *Pratylenchus brachyurus*, *Pratylenchus zeae*,  
30 *Procornitermes triacifer*, *Pseudocercospora personata*, *Pseudoperonospora cubensis*,  
*Puccinia horiana*, *Puccinia psidii*, *Puccinia trititica*, *Pyricularia grisea*, *Ramularia areola*,  
*Rhizoctonia solani*, *Rhopalosiphum graminum*, *Rhopalosiphum maidis*, *Rhopalosiphum rufiabdominale*,  
*Sclerotinia sclerotiorum*, *Septoria glycines*, *Septoria lactucae*, *Septoria*

*lycopersici*, *Septoria tritici*, *Sphaerotheca fuliginea*, *Sphaerotheca pannosa*, *sphenophorus levis*, *Spodoptera eridania*, *Spodoptera frugiperda*, *Stagonospora nodorum*, *Sternechus subsignatus*, *Syntermes molestus*, *Thrips tabaci*, *Tranzschelia discolor*, *Uromyces alstroemeriae*, *Uromyces appendiculatus* and *Ceratocystis paradoxa*.

5           The composition and method of the present invention are suitable for the treatment of plants of a wide range of valuable and desirable crops, including but not limited to: cereals, including wheat, barley, rye, oats, maize, rice, sorghum, triticale and related crops; beet, such as sugar beet and fodder beet; fruit, such as pomes, stone fruit and soft fruit, such as apples, grapes, pears, plums, peaches, almonds, cherries, and berries, for example strawberries,  
10 raspberries and blackberries; leguminous plants, such as drybeans, lentils, peas and soybeans; oil plants, such as rape, mustard and sunflowers; cucurbitaceae, such as marrows, cucumbers and melons; fibre plants, for example cotton, flax, hemp and jute; citrus, such as oranges, lemons, grapefruit and mandarins; vegetables, for example spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes and paprika; coffee; sugarcane; as well as  
15 ornamentals, including flowers, such as rose, shrubs, broad-leaved trees and evergreens, such as conifers.

In certain embodiments, the composition and method of the present invention are employed in the treatment of cereals, fibre plants, leguminous plants and sugarcane.

20           The composition and method of the present invention find particularly advantageous use in the treatment of crops of maize, rice, wheat, soybean, cotton and sugarcane.

25           The synergistic combination comprising (A) an insecticidal component comprising fipronil and thiodicarb; and (B) a fungicidal component comprising azoxystrobin and carbendazim, is particularly effective in preventing, controlling and/or treating of insect, nematode and fungal infestations as mentioned above in maize, rice, wheat, soybean, cotton and sugarcane, their plant parts and/or surroundings.

30           The rates of application (use) of the components of the combination of the present invention may vary, for example, according to the degree of control required, type of use, type of crop, the specific active compounds in the combination, type of plants, but is such that the active compounds in the combination in an effective amount to provide the desired action (such as insects, nematode or fungal control). The application rate of the composition for a given set of conditions can readily be determined by trials.

In general the components of the combination of the present invention can be applied to plants or their locus at an application rate of from about 0.1 kilograms/hectare (kg/ha) to about 4 kg/ha, based on the total amount of active ingredient (component (A) + component (B)). An application rate of between about 0.1 kg of active ingredient (a.i.)/ha and 1.5 kg a.i./ha is preferred. For treatment of propagation materials, such as seed treatment, the application rate may be between about 10 g a.i./100kg of propagation material, such as seeds, and about 700 g a.i./100kg of propagation material, preferably about 100 g a.i./100kg of propagation material and about 500 g a.i./100kg of propagation material, based on the total amount of active ingredient (component (A) + component (B)).

The compositions used in the present invention are useful as insecticides, nematocides and fungicides, demonstrating synergistic activity for preventing, controlling and/or treating insects, nematodes and fungal infestations. The compositions can be formulated in the same manner in which insecticides, nematocides and fungicides are generally formulated. The compounds may be applied either separately or combined as part of a two-part system, three-part or four-part.

The components (A1), (A2), (B1) and (B2) may be applied in any desired sequence, any combination, consecutively or simultaneously.

In the event components (A1), (A2), (B1) and (B2) are applied simultaneously in the present invention, they may be applied as a composition containing the components, in which case components (A1), (A2), (B1) and (B2) can be obtained from a separate formulation source and mixed together (known as a tank-mix, ready-to-apply, spray broth, or slurry), optionally with other pesticides. Alternatively, components (A1), (A2), (B1) and (B2) can be obtained as a single formulation mixture source (known as a pre-mix, concentrate, formulated compound (or product)), and optionally mixed together with other pesticides.

The components (A1), (A2), (B1) and (B2) of the present invention can be applied in a variety of ways known to those skilled in the art, at various concentrations. The compositions are useful in preventing, controlling and/or treating insect, nematode and fungal infestations in plants, plant parts and/or surroundings by pre-emergence or post-emergence application to plants, plant parts and/or surroundings is desired.

The present invention may employ compositions in a wide range of different formulations. The compositions for use in the present invention may thus be formulated as:

a water-soluble concentrate (SL), an emulsifiable concentrate (EC), an emulsion (EW), a micro-emulsion (ME), a suspension concentrates (SC), an oil-based suspension concentrate (OD), a flowable suspension (FS), water-dispersible granules (WG), water-soluble granules (SG), a water-dispersible powder (WP), a water soluble powder (SP), granules (GR),  
5 encapsulated granules (CG), fine granules (FG), macrogranules (GG), an aqueous suspo-emulsion (SE), a microencapsulated suspension (CS), and microgranules (MG). Preferred formulation types include a suspension concentrate (SC) and a flowable suspension (FS).

Using such formulations, either straight (that is undiluted) or diluted with a suitable solvent, especially water, plants, plant parts and/or the surroundings can be treated and  
10 protected against insect, nematode and fungi by spraying, pouring immersing or treating. Generally, the formulation can be diluted with water at the rate of about 100mL to 5L of composition in 1L to 100L of water.

In some embodiments, the composition is formulated as a suspension concentrate (SC). For SC formulations, the composition can be diluted with water at the rate of 0.5 to 2L  
15 of composition in 100L of water. For flowable suspension (FS) formulations, the composition can be diluted with water at a rate of 1L of composition in 1 to 4L of water.

In the practice of the present invention, the compositions can be applied using methods known in the art. These methods include coating, spraying, dipping, soaking, injection, irrigation and the like, which will be well known to the person skilled in the art.

Further, other biocidally active ingredients or compositions may be combined with the  
20 components (A1), (A2), (B1) and (B2) of this invention. For example, the invention may employ, in addition to components (A1), (A2), (B1) and (B2), one or more herbicides, insecticides, fungicides, bactericides, acaricides or nematocides, in order to broaden the spectrum of activity. The components (A1), (A2), (B1) and (B2) used in the present  
25 invention are distinguished by the fact that they are especially well tolerated by plants and are environmentally friendly.

As one skilled in the art is aware, in insect, nematode and fungal testing, a significant number of factors that are not readily controllable can affect the results of individual tests and render them non-reproducible. For example, the results may vary depending on  
30 environmental factors, such as amount of sunlight and water, soil type, pH of the soil, temperature, and humidity, among other factors. Also, the depth of planting, the application rate of individual and combined insecticides and fungicides, and the ratio of each insecticide

and fungicide, as well as the nature of crops or weeds being tested, can affect the results of the test. Results may vary from crop to crop within the crop varieties.

The following examples are given by way of illustration and not by way of limitation  
5 of the invention.

Unless otherwise indicated, percentages are weight percent.

### **FORMULATION EXAMPLES**

Examples 1 to 14, 16 and 17 are examples of compositions which may be employed  
in the method and use of the present invention. Examples 15 and 18 to 23 are examples of  
10 compositions of the present invention and compositions which may be employed in the  
method and use of the present invention.

#### Example 1 – 5% Fipronil flowable suspension (FS) formulation

15 A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

#### Example 2 – 25% Thiodicarb flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Thiodicarb                                            | 25%             |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

#### 5 Example 3 – 0.6% Azoxystrobin flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Azoxystrobin                                          | 0.6%            |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.2%            |
| NIPACIDE BIT 20                                       | 0.2%            |
| Water                                                 | Balance to 100% |

Example 4 - 5% Carbendazim flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.2%            |
| NIPACIDE BIT 20                                       | 0.2%            |
| Water                                                 | Balance to 100% |

5

Example 5 – 5% Fipronil + 25% Thiodicarb flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

10

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 5%              |
| Thiodicarb                                            | 25%             |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.2%            |
| NIPACIDE BIT 20                                       | 0.2%            |
| Water                                                 | Balance to 100% |

Example 6 – 5% Fipronil + 0.6% Azoxystrobin flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

5

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 5%              |
| Azoxystrobin                                          | 0.6%            |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.2%            |
| NIPACIDE BIT 20                                       | 0.2%            |
| Water                                                 | Balance to 100% |

10

Example 7 – 5% Fipronil + 5% Carbendazim flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

15

|                             |     |
|-----------------------------|-----|
| Fipronil                    | 5%  |
| Carbendazim                 | 5%  |
| Propylene glycol            | 10% |
| Tristyrylphenol ethoxylates | 5%  |

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 8 – 25% Thiodicarb + 0.6% Azoxystrobin flowable suspension (FS) formulation

5 A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Thiodicarb                                            | 25%             |
| Azoxystrobin                                          | 0.6%            |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 9 – 25% Thiodicarb + 5% Carbendazim flowable suspension (FS) formulation

10

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Thiodicarb                                            | 25%             |
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 1%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

5 Example 10 – 0.6% Azoxystrobin + 5% Carbendazim flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Azoxystrobin                                          | 0.6%            |
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 11 – 5% Fipronil + 25% Thiodicarb + 0.6% Azoxystrobin flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

5

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 5%              |
| Thiodicarb                                            | 25%             |
| Azoxystrobin                                          | 0.6%            |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 12 – 5% Fipronil + 25% Thiodicarb + 5% Carbendazim flowable suspension (FS) formulation

10

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |     |
|-------------------------------------------------------|-----|
| Fipronil                                              | 5%  |
| Thiodicarb                                            | 25% |
| Carbendazim                                           | 5%  |
| Propylene glycol                                      | 10% |
| Tristyrylphenol ethoxylates                           | 5%  |
| Sodium lignosulfonate                                 | 2%  |
| Carboxymethylcellulose                                | 1%  |
| Silicone oil (in the form of a 75% emulsion in water) | 1%  |
| PVP K-30                                              | 1%  |

|                 |                 |
|-----------------|-----------------|
| Pigment         | 2%              |
| Xanthan gum     | 0.1%            |
| NIPACIDE BIT 20 | 0.1%            |
| Water           | Balance to 100% |

Example 13 – 5% Fipronil + 0.6% Azoxystrobin + 5% Carbendazim flowable suspension (FS) formulation

5

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 5%              |
| Azoxystrobin                                          | 0.6%            |
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

10 Example 14 – 25% Thiodicarb + 0.6% Azoxystrobin + 5% Carbendazim flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

|            |     |
|------------|-----|
| Thiodicarb | 25% |
|------------|-----|

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Azoxystrobin                                          | 0.6%            |
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 15 – 5% Fipronil + 25% Thiodicarb + 0.6% Azoxystrobin + 5% Carbendazim flowable suspension (FS) formulation

5

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 5%              |
| Thiodicarb                                            | 25%             |
| Azoxystrobin                                          | 0.6%            |
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 16 – 5% Fipronil + 25% Thiodicarb suspension concentrate (SC) formulation

A suspension concentrate (SC) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 5%              |
| Thiodicarb                                            | 25%             |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

5

Example 17 – 0.6% Azoxystrobin + 5% Carbendazim suspension concentrate (SC) formulation

10 A suspension concentrate (SC) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Azoxystrobin                                          | 0.6%            |
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 18 – 5% Fipronil + 25% Thiodicarb + 0.6% Azoxystrobin + 5% Carbendazim suspension concentrate (SC) formulation

5 A suspension concentrate (SC) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 5%              |
| Thiodicarb                                            | 25%             |
| Azoxystrobin                                          | 0.6%            |
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 19 – 7% Fipronil + 35% Thiodicarb + 0.8% Azoxystrobin + 7% Carbendazim flowable suspension (FS) formulation

10

A flowable suspension (FS) formulation was prepared from the following components:

|                             |      |
|-----------------------------|------|
| Fipronil                    | 7%   |
| Thiodicarb                  | 35%  |
| Azoxystrobin                | 0.8% |
| Carbendazim                 | 7%   |
| Propylene glycol            | 10%  |
| Tristyrylphenol ethoxylates | 5%   |
| Sodium lignosulfonate       | 2%   |

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

Example 20 – 10% Fipronil + 50% Thiodicarb + 1.2% Azoxystrobin + 10% Carbendazim flowable suspension (FS) formulation

5

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 10%             |
| Thiodicarb                                            | 50%             |
| Azoxystrobin                                          | 1.2%            |
| Carbendazim                                           | 10%             |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

10 Example 21 – 1% Fipronil + 50% Thiodicarb + 2.5% Azoxystrobin + 1% Carbendazim flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 1%              |
| Thiodicarb                                            | 50%             |
| Azoxystrobin                                          | 2.5%            |
| Carbendazim                                           | 1%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

5

Example 22 – 5% Fipronil + 40% Thiodicarb + 0.1% Azoxystrobin + 1% Carbendazim flowable suspension (FS) formulation

A flowable suspension (FS) formulation was prepared from the following components:

10

|                                                       |      |
|-------------------------------------------------------|------|
| Fipronil                                              | 5%   |
| Thiodicarb                                            | 40%  |
| Azoxystrobin                                          | 0.1% |
| Carbendazim                                           | 1%   |
| Propylene glycol                                      | 10%  |
| Tristyrylphenol ethoxylates                           | 5%   |
| Sodium lignosulfonate                                 | 2%   |
| Carboxymethylcellulose                                | 1%   |
| Silicone oil (in the form of a 75% emulsion in water) | 1%   |
| PVP K-30                                              | 1%   |
| Pigment                                               | 2%   |

|                 |                 |
|-----------------|-----------------|
| Xanthan gum     | 0.1%            |
| NIPACIDE BIT 20 | 0.1%            |
| Water           | Balance to 100% |

Example 23 – 1% Fipronil + 30% Thiodicarb + 1% Azoxystrobin + 5% Carbendazim flowable suspension (FS) formulation

5

A flowable suspension (FS) formulation was prepared from the following components:

|                                                       |                 |
|-------------------------------------------------------|-----------------|
| Fipronil                                              | 1%              |
| Thiodicarb                                            | 30%             |
| Azoxystrobin                                          | 1%              |
| Carbendazim                                           | 5%              |
| Propylene glycol                                      | 10%             |
| Tristyrylphenol ethoxylates                           | 5%              |
| Sodium lignosulfonate                                 | 2%              |
| Carboxymethylcellulose                                | 1%              |
| Silicone oil (in the form of a 75% emulsion in water) | 1%              |
| PVP K-30                                              | 1%              |
| Pigment                                               | 2%              |
| Xanthan gum                                           | 0.1%            |
| NIPACIDE BIT 20                                       | 0.1%            |
| Water                                                 | Balance to 100% |

10

## BIOLOGICAL EXAMPLES

### FIELD TEST 1 - SOYBEAN - *MELOIDOGYNE JAVANICA* - NEMATODE

15 A nematode inoculum was prepared from a pure subpopulation of *Meloidogyne javanica* kept from tomato (*Solanum lycopersicom L.*) in clay recipients in a greenhouse. The subpopulation was previously identified based on morphological characters of perineal patterns prepared as per TAYLOR & NETSCHER (1974), on the morphology of the mouth

region of males (EISENBACK et al., 1981), and on the isoenzymatic phenotype for esterase obtained by the technique by ESBENSHADE & TRIANTAPHYLLOU (1990), using a traditional vertical electrophoresis system, namely Mini Protean II by BIO-RAD.

A suspension containing eggs and second stage juveniles (J2) was prepared from the tomato roots. 10mL of the suspension was inoculated with eggplant for 22 days. Thereafter, the eggplant was transplanted into a pot and kept in the greenhouse. After 100 days, the roots of the eggplant were washed and ground in a blender with a solution of 0.5% sodium hypochlorite. The suspension was then passed through a sieve of 200 mesh (0.074 mm openings) on 500 (0.025 mm openings). The eggs and juveniles retained on the 500 mesh sieve were collected and washed.

Soybean seeds were treated with the formulations of Examples 1 to 15. The seeds were then inoculated with 3 mL of a suspension containing 3,000 eggs and second stage juveniles of *Meloidogyne javanica*. Thereafter the seeds were sown.

The number of galls on 10 grams of roots of the soybean plants was counted 50 days after sowing. The results are set out in Table 1 below.

Table 1.

| Test                     | Fipronil<br>(g/100kg of<br>seeds) | Thiodicarb<br>(g/100kg of<br>seeds) | Azoxystrobin<br>(g/100kg of<br>seeds) | Carbendazim<br>(g/100kg of<br>seeds) | Number<br>of galls<br>on 10<br>grams of<br>roots |
|--------------------------|-----------------------------------|-------------------------------------|---------------------------------------|--------------------------------------|--------------------------------------------------|
| Control                  | 0                                 | 0                                   | 0                                     | 0                                    | 15                                               |
| Formulation<br>Example 1 | 25                                | 0                                   | 0                                     | 0                                    | 15                                               |
| Formulation<br>Example 2 | 0                                 | 125                                 | 0                                     | 0                                    | 13                                               |
| Formulation<br>Example 3 | 0                                 | 0                                   | 3                                     | 0                                    | 15                                               |
| Formulation<br>Example 4 | 0                                 | 0                                   | 0                                     | 25                                   | 15                                               |

|                        |    |     |   |    |    |
|------------------------|----|-----|---|----|----|
| Formulation Example 5  | 25 | 125 | 0 | 0  | 8  |
| Formulation Example 6  | 25 | 0   | 3 | 0  | 14 |
| Formulation Example 7  | 25 | 0   | 0 | 25 | 14 |
| Formulation Example 8  | 0  | 125 | 3 | 0  | 13 |
| Formulation Example 9  | 0  | 125 | 0 | 25 | 11 |
| Formulation Example 10 | 0  | 0   | 3 | 25 | 14 |
| Formulation Example 11 | 25 | 125 | 3 | 0  | 7  |
| Formulation Example 12 | 25 | 125 | 0 | 25 | 4  |
| Formulation Example 13 | 25 | 0   | 3 | 25 | 6  |
| Formulation Example 14 | 0  | 125 | 3 | 25 | 5  |
| Formulation Example 15 | 25 | 125 | 3 | 25 | 0  |

### FIELD TEST 2 - SOYBEAN - *PHYLLOPHAGA CUYABANA* (BEETLES)

Soybean seeds were treated with the formulations of Examples 1 to 15 and planted.

- 5 Beetles (*Phyllophaga cuyabana*) were reared in the laboratory. The number of beetles was counted, collected and then put on the planting area. The remaining population of beetle was examined 10 days after sowing. The results are set out in Table 2 below.

Table 2.

| <b>Test</b>               | <b>Fipronil<br/>(g/100kg<br/>of seeds)</b> | <b>Thiodicarb<br/>(g/100kg of<br/>seeds)</b> | <b>Azoxystrobin<br/>(g/100kg of<br/>seeds)</b> | <b>Carbendazim<br/>(g/100kg of seeds)</b> | <b>The<br/>remaining<br/>population<br/>of beetle<br/>(%)</b> |
|---------------------------|--------------------------------------------|----------------------------------------------|------------------------------------------------|-------------------------------------------|---------------------------------------------------------------|
| Control                   | 0                                          | 0                                            | 0                                              | 0                                         | 75                                                            |
| Formulation<br>Example 1  | 25                                         | 0                                            | 0                                              | 0                                         | 58                                                            |
| Formulation<br>Example 2  | 0                                          | 125                                          | 0                                              | 0                                         | 48                                                            |
| Formulation<br>Example 3  | 0                                          | 0                                            | 3                                              | 0                                         | 73                                                            |
| Formulation<br>Example 4  | 0                                          | 0                                            | 0                                              | 25                                        | 73                                                            |
| Formulation<br>Example 5  | 25                                         | 125                                          | 0                                              | 0                                         | 40                                                            |
| Formulation<br>Example 6  | 25                                         | 0                                            | 3                                              | 0                                         | 58                                                            |
| Formulation<br>Example 7  | 25                                         | 0                                            | 0                                              | 25                                        | 55                                                            |
| Formulation<br>Example 8  | 0                                          | 125                                          | 3                                              | 0                                         | 47                                                            |
| Formulation<br>Example 9  | 0                                          | 125                                          | 0                                              | 25                                        | 45                                                            |
| Formulation<br>Example 10 | 0                                          | 0                                            | 3                                              | 25                                        | 65                                                            |
| Formulation<br>Example 11 | 25                                         | 125                                          | 3                                              | 0                                         | 20                                                            |
| Formulation<br>Example 12 | 25                                         | 125                                          | 0                                              | 25                                        | 15                                                            |
| Formulation<br>Example 13 | 25                                         | 0                                            | 3                                              | 25                                        | 30                                                            |
| Formulation<br>Example 14 | 0                                          | 125                                          | 3                                              | 25                                        | 18                                                            |

|                           |    |     |   |    |   |
|---------------------------|----|-----|---|----|---|
| Formulation<br>Example 15 | 25 | 125 | 3 | 25 | 5 |
|---------------------------|----|-----|---|----|---|

### FIELD TEST 3 – SOYBEAN - *CERCOSPORA KIKUCHII*

Young soybean plants were treated with formulations of Examples 16 to 18, sprayed with a conidial suspension of *Cercospora kikuchii*, and incubated at 20°C and 100% relative atmospheric humidity for 48 hours. After remaining in a greenhouse at 15°C and 80% relative atmospheric humidity for 15 days, the severity of the damage to the young soybean plants was assessed. The results are set out in Table 3 below.

Table 3.

| Test                      | Fipronil<br>(g/ha) | Thiodicarb<br>(g/ha) | Azoxystrobin<br>(g/ha) | Carbendazim<br>(g/ha) | Severity<br>(%) |
|---------------------------|--------------------|----------------------|------------------------|-----------------------|-----------------|
| Control                   | 0                  | 0                    | 0                      | 0                     | 80              |
| Formulation<br>Example 16 | 200                | 1000                 | 0                      | 0                     | 80              |
| Formulation<br>Example 17 | 0                  | 0                    | 24                     | 200                   | 25              |
| Formulation<br>Example 18 | 200                | 1000                 | 24                     | 200                   | 0               |

### FIELD TEST 4 – SOYBEAN - STEM ROT (*SCLEROTINIA SCLEROTIORUM*)

Young soybean plants were treated with formulations of Examples 16 to 18, sprayed with a conidial suspension of *Sclerotinia sclerotiorum*, and incubated at 20°C and 100% relative atmospheric humidity for 48 hours. After remaining in a greenhouse at 15°C and 80% relative atmospheric humidity for 15 days the severity of the damage to the young soybean plants was assessed. The results are set out in Table 4 below.

Table 4.

| Test                      | Fipronil<br>(g/ha) | Thiodicarb<br>(g/ha) | Azoxystrobin<br>(g/ha) | Carbendazim<br>(g/ha) | Severity<br>(%) |
|---------------------------|--------------------|----------------------|------------------------|-----------------------|-----------------|
| Control                   | 0                  | 0                    | 0                      | 0                     | 80              |
| Formulation<br>Example 16 | 200                | 1000                 | 0                      | 0                     | 65              |
| Formulation<br>Example 17 | 0                  | 0                    | 24                     | 200                   | 25              |
| Formulation<br>Example 18 | 200                | 1000                 | 24                     | 200                   | 0               |

#### 5 FIELD TEST 5 – SUGARCANE - *MELOIDOGYNE JAVANICA* - NEMATODE

A nematode inoculum was prepared from a pure subpopulation of *Meloidogyne javanica* kept in soybean plants (*Glycine max* L.) in clay recipients in a greenhouse. The subpopulation was previously identified based on morphological characters of perineal patterns prepared as per TAYLOR & NETSCHER (1974), on the morphology of the mouth region of males (EISENBACK et al., 1981), and on the isoenzymatic phenotype for esterase obtained by the technique by ESBENSHADE & TRIANTAPHYLLOU (1990), using a traditional vertical electrophoresis system, namely Mini Protean II by BIO-RAD.

3mL samples of the formulations Examples 16 to 18 were applied uniformly on the soil and around the roots at the rates indicated in Table 5 below. Thereafter, the roots of the sugarcane plants were inoculated with 10mL of a suspension containing 3000 eggs (*Meloidogyne javanica*) and second-stage juveniles of *Meloidogyne javanica*, after which the roots were covered with soil.

The number of *Meloidogyne javanica* in various developmental stages in 10 grams of roots was counted 100 days after application. The results are set out in Table 5 below.

Table 5.

| Test                      | Fipronil<br>(g/ha) | Thiodicarb<br>(g/ha) | Azoxystrobin<br>(g/ha) | Carbendazim<br>(g/ha) | Number of<br><i>Meloidogyne javanica</i> in<br>various<br>development<br>stages in 10<br>grams of roots |
|---------------------------|--------------------|----------------------|------------------------|-----------------------|---------------------------------------------------------------------------------------------------------|
| Control                   | 0                  | 0                    | 0                      | 0                     | 268                                                                                                     |
| Formulation<br>Example 16 | 200                | 1000                 | 0                      | 0                     | 53                                                                                                      |
| Formulation<br>Example 17 | 0                  | 0                    | 24                     | 200                   | 245                                                                                                     |
| Formulation<br>Example 18 | 200                | 1000                 | 24                     | 200                   | 6                                                                                                       |

#### FIELD TEST 6 – SUGARCANE - *HETEROTERMES TENUIS* - TERMITE

Termites (*Heterotermes tenuis*) were reared in the laboratory. The number of termites was counted, the termites collected and then put on healthy young sugarcane plants. Formulations of Examples 16 to 18 were diluted with water and then applied to the soil around the plants. After remaining in a greenhouse at 21 to 25°C and 80% relative atmospheric humidity for 10 days, the remaining population of termites was examined. The results are set out in Table 6 below.

10

15 Table 6.

| Test | Fipronil<br>(g/ha) | Thiodicarb<br>(g/ha) | Azoxystrobin<br>(g/ha) | Carbendazim<br>(g/ha) | The remaining<br>population of<br>termite (%) |
|------|--------------------|----------------------|------------------------|-----------------------|-----------------------------------------------|
|------|--------------------|----------------------|------------------------|-----------------------|-----------------------------------------------|

|                        |     |      |    |     |    |
|------------------------|-----|------|----|-----|----|
| Control                | 0   | 0    | 0  | 0   | 80 |
| Formulation Example 16 | 200 | 1000 | 0  | 0   | 50 |
| Formulation Example 17 | 0   | 0    | 24 | 200 | 75 |
| Formulation Example 18 | 200 | 1000 | 24 | 200 | 5  |

#### FIELD TEST 7- SUGARCANE - *SPHENOPHORUS LEVI* (BEETLES)

Beetles (*Sphenophorus Levi*) were reared in the laboratory. The number of beetles was counted, the beetles collected and then put on healthy young sugarcane plants. The formulations of Examples 16 to 18 were diluted with water and then applied to the soil around the plants. After remaining in a greenhouse at 21 to 25°C and 80% relative atmospheric humidity for 10 days, the remaining population of beetles was examined. The results are set out in Table 7 below.

10

Table 7.

| Test    | Fipronil (g/ha) | Thiodicarb (g/ha) | Azoxystrobin (g/ha) | Carbendazim (g/ha) | The remaining population of beetles (%) |
|---------|-----------------|-------------------|---------------------|--------------------|-----------------------------------------|
| Control | 0               | 0                 | 0                   | 0                  | 80                                      |

|                        |     |      |    |     |    |
|------------------------|-----|------|----|-----|----|
| Formulation Example 16 | 200 | 1000 | 0  | 0   | 55 |
| Formulation Example 17 | 0   | 0    | 24 | 200 | 70 |
| Formulation Example 18 | 200 | 1000 | 24 | 200 | 5  |

### FIELD TEST 8 – SUGARCANE - PINEAPPLE DISEASES

Young sugarcane plants were treated with formulations of Examples 16 to 18 and then sprayed with a conidial suspension of fungus complex (the major fungus being *Ceratocystis paradoxa* causing Pineapple diseases). The plants were incubated at 20°C and 100% relative atmospheric humidity for 48 hours. After remaining in a greenhouse at 15°C and 80% relative atmospheric humidity for 15 days the severity of the damage to the young soybean plants was assessed. The results are set out in Table 8 below.

10

Table 8.

| Test                   | Fipronil (g/ha) | Thiodicarb (g/ha) | Azoxystrobin (g/ha) | Carbendazim (g/ha) | Severity (%) |
|------------------------|-----------------|-------------------|---------------------|--------------------|--------------|
| Control                | 0               | 0                 | 0                   | 0                  | 80           |
| Formulation Example 16 | 200             | 1000              | 0                   | 0                  | 75           |
| Formulation Example 17 | 0               | 0                 | 24                  | 200                | 45           |
| Formulation Example 18 | 200             | 1000              | 24                  | 200                | 5            |

### FIELD TEST 9 – WHEAT - *MELOIDOGYNE JAVANICA* - NEMATODE

A nematode inoculum was prepared from a pure subpopulation of *Meloidogyne javanica* in tomato (*Solanum lycopersicom L.*) in clay recipients in a greenhouse. The subpopulation was previously identified based on morphological characters of perineal patterns, on the morphology of the mouth region, and on the isoenzymatic phenotype for esterase.

3mL samples of the formulations of Examples 16 to 18 were applied uniformly on the soil and around the roots at the rate indicated in Table 9 below. Thereafter, the roots of the wheat plants were inoculated with 10mL of a suspension containing *Meloidogyne javanica* in various developmental stages, after which the roots were covered with soil.

The number of galls on 10 grams of roots was measured 90 days after application. The results are set out in Table 9 below.

Table 9.

| Test                      | Fipronil<br>(g/ha) | Thiodicarb<br>(g/ha) | Azoxystrobin<br>(g/ha) | Carbendazim<br>(g/ha) | Number of<br>galls on 10<br>grams of<br>roots |
|---------------------------|--------------------|----------------------|------------------------|-----------------------|-----------------------------------------------|
| Control                   | 0                  | 0                    | 0                      | 0                     | 25                                            |
| Formulation<br>Example 16 | 200                | 1000                 | 0                      | 0                     | 14                                            |
| Formulation<br>Example 17 | 0                  | 0                    | 24                     | 200                   | 24                                            |
| Formulation<br>Example 18 | 200                | 1000                 | 24                     | 200                   | 2                                             |

#### FIELD TEST 10 – WHEAT - *METOPOLOPHIUM DIRHODUM* - APHID

Wheat seeds were treated with the formulations of Examples 1 to 15 and planted. Aphids (*Metopolophium Dirhodum*) were reared in the laboratory. The number of aphids was counted, there aphids were collected and then put on the planting area. The population of

aphids remaining 10 days after sowing was determined. The results are set out in Table 10 below.

Table 10.

| <b>Test</b>               | <b>Fipronil<br/>(g/100kg<br/>of seeds)</b> | <b>Thiodicarb<br/>(g/100kg of<br/>seeds)</b> | <b>Azoxystrobin<br/>(g/100kg of<br/>seeds)</b> | <b>Carbendazim<br/>(g/100kg of<br/>seeds)</b> | <b>The<br/>remaining<br/>population<br/>of Aphid<br/>(%)</b> |
|---------------------------|--------------------------------------------|----------------------------------------------|------------------------------------------------|-----------------------------------------------|--------------------------------------------------------------|
| Control                   | 0                                          | 0                                            | 0                                              | 0                                             | 75                                                           |
| Formulation<br>Example 1  | 25                                         | 0                                            | 0                                              | 0                                             | 65                                                           |
| Formulation<br>Example 2  | 0                                          | 125                                          | 0                                              | 0                                             | 70                                                           |
| Formulation<br>Example 3  | 0                                          | 0                                            | 3                                              | 0                                             | 75                                                           |
| Formulation<br>Example 4  | 0                                          | 0                                            | 0                                              | 25                                            | 74                                                           |
| Formulation<br>Example 5  | 25                                         | 125                                          | 0                                              | 0                                             | 50                                                           |
| Formulation<br>Example 6  | 25                                         | 0                                            | 3                                              | 0                                             | 65                                                           |
| Formulation<br>Example 7  | 25                                         | 0                                            | 0                                              | 25                                            | 60                                                           |
| Formulation<br>Example 8  | 0                                          | 125                                          | 3                                              | 0                                             | 55                                                           |
| Formulation<br>Example 9  | 0                                          | 125                                          | 0                                              | 25                                            | 55                                                           |
| Formulation<br>Example 10 | 0                                          | 0                                            | 3                                              | 25                                            | 75                                                           |
| Formulation<br>Example 11 | 25                                         | 125                                          | 3                                              | 0                                             | 40                                                           |
| Formulation<br>Example 12 | 25                                         | 125                                          | 0                                              | 25                                            | 30                                                           |

|                        |    |     |   |    |    |
|------------------------|----|-----|---|----|----|
| Formulation Example 13 | 25 | 0   | 3 | 25 | 45 |
| Formulation Example 14 | 0  | 125 | 3 | 25 | 35 |
| Formulation Example 15 | 25 | 125 | 3 | 25 | 10 |

### FIELD TEST 11– COTTON - *MELOIDOGYNE JAVANICA* - NEMATODE

A nematode inoculum was prepared from a pure subpopulation of *Meloidogyne javanica* in tomato (*Solanum lycopersicom L.*) in clay recipients in a greenhouse. The subpopulation was previously identified based on morphological characters of perineal patterns, on the morphology of the mouth region, and on the isoenzymatic phenotype for esterase.

3mL samples of the formulations of Examples 16 to 18 were applied uniformly on the soil and around the roots at the rate indicated in Table 11 below. Thereafter, the roots of the cotton plants were inoculated with 10mL of a suspension containing *Meloidogyne javanica* in various developmental stages, after which the roots were covered with soil.

The number of galls on 10 grams of roots was measured 90 days after application. The results are set out in Table 11 below.

Table 11.

| Test                   | Fipronil (g/ha) | Thiodicarb (g/ha) | Azoxystrobin (g/ha) | Carbendazim (g/ha) | Number of galls on 10 grams of roots |
|------------------------|-----------------|-------------------|---------------------|--------------------|--------------------------------------|
| Control                | 0               | 0                 | 0                   | 0                  | 22                                   |
| Formulation Example 16 | 200             | 1000              | 0                   | 0                  | 9                                    |
| Formulation Example 17 | 0               | 0                 | 24                  | 200                | 22                                   |
| Formulation            | 200             | 1000              | 24                  | 200                | 2                                    |

|            |  |  |  |  |  |
|------------|--|--|--|--|--|
| Example 18 |  |  |  |  |  |
|------------|--|--|--|--|--|

# **FIELD TEST 12 - COTTON - *ELASMOPALPUS LIGNOSELLUS* (SNOUT**

**5 MOTH)**

Cotton seeds were treated with the formulations of Examples 1 to 15 and then planted. Moths (*larvae*) (*Elasmopalpus lignosellus*) were reared in the laboratory. The number of larvae was counted, the larvae collected and then put on the planting area. The remaining population of larvae was examined 15 days after sowing. The results are set out in Table 12

**10** below.

Table 12.

| Test                     | Fipronil<br>(g/100kg of<br>seeds) | Thiodicarb<br>(g/100kg of<br>seeds) | Azoxystrobin<br>(g/100kg of<br>seeds) | Carbendazim<br>(g/100kg of<br>seeds) | The<br>remaining<br>population<br>of larvae<br>(%) |
|--------------------------|-----------------------------------|-------------------------------------|---------------------------------------|--------------------------------------|----------------------------------------------------|
| Control                  | 0                                 | 0                                   | 0                                     | 0                                    | 70                                                 |
| Formulation<br>Example 1 | 25                                | 0                                   | 0                                     | 0                                    | 55                                                 |
| Formulation<br>Example 2 | 0                                 | 125                                 | 0                                     | 0                                    | 45                                                 |
| Formulation<br>Example 3 | 0                                 | 0                                   | 3                                     | 0                                    | 70                                                 |
| Formulation<br>Example 4 | 0                                 | 0                                   | 0                                     | 25                                   | 65                                                 |
| Formulation<br>Example 5 | 25                                | 125                                 | 0                                     | 0                                    | 35                                                 |
| Formulation<br>Example 6 | 25                                | 0                                   | 3                                     | 0                                    | 55                                                 |
| Formulation<br>Example 7 | 25                                | 0                                   | 0                                     | 25                                   | 55                                                 |

|                        |    |     |   |    |    |
|------------------------|----|-----|---|----|----|
| Formulation Example 8  | 0  | 125 | 3 | 0  | 45 |
| Formulation Example 9  | 0  | 125 | 0 | 25 | 43 |
| Formulation Example 10 | 0  | 0   | 3 | 25 | 68 |
| Formulation Example 11 | 25 | 125 | 3 | 0  | 35 |
| Formulation Example 12 | 25 | 125 | 0 | 25 | 30 |
| Formulation Example 13 | 25 | 0   | 3 | 25 | 50 |
| Formulation Example 14 | 0  | 125 | 3 | 25 | 40 |
| Formulation Example 15 | 25 | 125 | 3 | 25 | 5  |

### FIELD TEST 13 - WHEAT - *ELASMOPALPUS LIGNOSELLUS* (MOTH)

Moths (*larvae*) (*Elasmopalus lignosellus*) were reared in the laboratory. The number of larvae was counted, the larvae collected and then put on healthy young wheat plants. The formulations of Examples 16 to 18 were diluted with water and then sprayed on to the plants. After remaining in a greenhouse at 21 to 25°C and 80% relative atmospheric humidity for 10 days, the remaining population of larvae was examined. The results are set out in Table 13 below.

Table 13.

| Test    | Fipronil (g/ha) | Thiodicarb (g/ha) | Azoxystrobin (g/ha) | Carbendazim (g/ha) | The remaining population of larvae (%) |
|---------|-----------------|-------------------|---------------------|--------------------|----------------------------------------|
| Control | 0               | 0                 | 0                   | 0                  | 95                                     |

|                        |     |      |    |     |    |
|------------------------|-----|------|----|-----|----|
| Formulation Example 16 | 200 | 1000 | 0  | 0   | 60 |
| Formulation Example 17 | 0   | 0    | 24 | 200 | 90 |
| Formulation Example 18 | 200 | 1000 | 24 | 200 | 10 |

#### FIELD TEST 14 - SOYBEAN - *ELASMOPALPUS LIGNOSELLUS* (SNOUT MOTH)

- 5 Soybean seeds were treated with the formulations of Examples 15, and 19 to 23, after which the seeds were planted. Moths (*larvae*) (*Elasmopalpus lignosellus*) were reared in the laboratory. The number of larvae was counted, the larvae collected and then put on the planting area. The population of larvae remaining 15 days after sowing was examined. The results are set out in Table 14 below.

10

Table 14.

| Test                   | Fipronil<br>(g/100kg of seeds) | Thiodicarb<br>(g/100kg of seeds) | Azoxystrobin<br>(g/100kg of seeds) | Carbendazim<br>(g/100kg of seeds) | The remaining population of larvae (%) |
|------------------------|--------------------------------|----------------------------------|------------------------------------|-----------------------------------|----------------------------------------|
| Control                | 0                              | 0                                | 0                                  | 0                                 | 85                                     |
| Formulation Example 15 | 25                             | 125                              | 3                                  | 25                                | 0                                      |
| Formulation Example 19 | 25                             | 125                              | 3                                  | 25                                | 0                                      |
| Formulation Example 20 | 25                             | 125                              | 3                                  | 25                                | 0                                      |
| Formulation Example 21 | 10                             | 500                              | 25                                 | 10                                | 5                                      |
| Formulation Example 22 | 50                             | 400                              | 1                                  | 10                                | 5                                      |

|                           |    |     |    |    |    |
|---------------------------|----|-----|----|----|----|
| Formulation<br>Example 23 | 10 | 300 | 10 | 50 | 10 |
|---------------------------|----|-----|----|----|----|

The results set out in the tables above show that the components (A1), (A2), (B1) and (B2) when employed in combination according to the present invention exhibit a surprisingly and unexpectedly high activity in the control of the infestations. The results demonstrate that the components (A1), (A2), (B1) and (B2) exhibit a clear and significant synergy.

All publications, patents and patent applications cited in this specification are herein incorporated by reference as if each individual publication or patent application were specifically and individually indicated to be incorporated by reference. Although the foregoing invention has been described in some detail by way of illustration and example for purposes of clarity of understanding, it will be readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes and modifications may be made thereto without departing from the spirit or scope of the appended claims.

Throughout the specification and the claims that follow, unless the context requires otherwise, the words “comprise” and “include” and variations such as “comprising” and “including” will be understood to imply the inclusion of a stated integer or group of integers, but not the exclusion of any other integer or group of integers.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgement of any form of suggestion that such prior art forms part of the common general knowledge.

## CLAIMS

1. A composition comprising:  
(A) an insecticidal component comprising:  
5 (A1) fipronil; and  
(A2) thiodicarb;  
and  
(B) a fungicidal component comprising:  
(B1) azoxystrobin; and  
10 (B2) carbendazim.
2. The composition according to claim 1, wherein the total amount of components (A) and (B) in the composition is from 1 to 95% by weight.
- 15 3. The composition according to either of claims 1 or 2, wherein component (A) is present in the composition in an amount of from 5 to 95% by weight.
4. The composition according to any preceding claim, wherein fipronil is present in the composition in an amount of from 1 to 30% by weight.  
20
5. The composition according to any preceding claim wherein thiodicarb is present in the composition in an amount of from 5 to 80% by weight.
6. The composition according to any preceding claim, wherein component (B) is present  
25 in the composition in an amount of from 1 to 50% by weight.
7. The composition according to any preceding claim, wherein azoxystrobin is present in the composition in an amount of from 0.1 to 15% by weight.

8. The composition according to any preceding claim wherein carbendazim is present in the composition in an amount of from 1 to 30% by weight.

5 9. The composition according to any preceding claim, wherein the weight ratio of component (A) to component (B) is from 50:1 to 1:50.

10. The composition according to claim 9, wherein the weight ratio of component (A) to component (B) is from 1.1:1 to 50:1.

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11. The composition according to any preceding claim, wherein the weight ratio of fipronil to thiodicarb is from 15:1 to 1:15.

12. The composition according to any preceding claim, wherein the weight ratio of  
15 azoxystrobin to carbendazim is from 20:1 to 1:20.

13. The composition according to any preceding claim, further comprising one or more auxiliary components selected from extenders, carriers, solvents, surfactants, stabilizers, anti-foaming agents, anti-freezing agents, preservatives, antioxidants, colorants, thickeners, solid  
20 adherents and inert fillers.

14. The composition according to any preceding claim, wherein the composition is formulated as a water-soluble concentrate (SL), an emulsifiable concentrate (EC), an emulsion (EW), a micro-emulsion (ME), a suspension concentrates (SC), an oil-based  
25 suspension concentrate (OD), a flowable suspension (FS), water-dispersible granules (WG), water-soluble granules (SG), a water-dispersible powder (WP), a water soluble powder (SP), granules (GR), encapsulated granules (CG), fine granules (FG), macrogranules (GG), an aqueous suspo-emulsion (SE), a microencapsulated suspension (CS), and microgranules (MG).

15. The composition according to claim 14, wherein the composition is a suspension concentrate (SC) or a flowable suspension (FS).

16. A method of preventing, controlling and/or treating insecticidal, nematode and fungicidal infestations in plants, the method comprising applying to the plants, their locus and/or plant propagation materials the components:

(A) an insecticidal component comprising:

(A1) fipronil; and

(A2) thiodicarb;

and

(B) a fungicidal component comprising:

(B1) azoxystrobin; and

(B2) carbendazim.

17. The method according to claim 16, wherein the weight ratio of component (A) to component (B) is from 50:1 to 1:50.

18. The method according to claim 17, wherein the weight ratio of component (A) to component (B) is from 1.1:1 to 50:1.

19. The method according to any of claims 16 to 18, wherein the weight ratio of fipronil to thiodicarb is from 15:1 to 1:15.

20. The method according to any of claims 16 to 19, wherein the weight ratio of azoxystrobin to carbendazim is from 20:1 to 1:20.

21. The method according to any of claims 16 to 19, wherein two or more of the components (A1), (A2), (B1) and (B2) are employed separately.

22. The method according to claim 21, wherein the components (A1), (A2), (B1) and (B2) are employed in two or more separate compositions.

23. The method according to any of claims 16 to 19, wherein the components (A1), (A2), (B1) and (B2) are employed simultaneously.

24. The method according to claim 23, wherein a single composition comprising components (A1), (A2), (B1) and (B2) is employed.

25. The method according to claim 24, wherein the composition is formulated as a water-soluble concentrate (SL), an emulsifiable concentrate (EC), an emulsion (EW), a micro-emulsion (ME), a suspension concentrates (SC), an oil-based suspension concentrate (OD), a flowable suspension (FS), water-dispersible granules (WG), water-soluble granules (SG), a water-dispersible powder (WP), a water soluble powder (SP), granules (GR), encapsulated granules (CG), fine granules (FG), macrogranules (GG), an aqueous suspo-emulsion (SE), a microencapsulated suspension (CS), and microgranules (MG).

20

26. The method according to claim 25, wherein the composition is a suspension concentrate (SC) or a flowable suspension (FS).

27. The method according to any of claims 24 to 26, wherein a composition according to any of claims 1 to 15 is employed.

25

28. The method according to any of claims 16 to 27, wherein the components (A) and (B) are applied to the plants and/or the locus of the plants at a rate of from 0.1 to 4 kg/ha.

29. The method according to any of claims 16 to 28, wherein the components (A) and (B) are applied to the plant propagation material at a rate of from 10 to 700 g/100kg.

30. The method according to any of claims 16 to 29, wherein the species being controlled is one or more selected from *Alabama argillacea*, *Alternaria brassicae*, *Alternaria dauci*, *Alternaria porri*, *Alternaria solani*, *Anticarsia gemmatilis*, *Aphis gossypii*, *Aracanthus mourei*, *Aspergillus flavus*, *Aspergillus spp.*, *Asperisporium caricae*, *Atta capiguara*, *Bemisia tabaci*, *Bipolaris sorokiniana*, *Cercospora arachidicola*, *Cercospora beticola*, *Cercospora coffeicola*, *Cercospora kikuchii*, *Cercospora sojae*, *Cerotelium fici*, *Colletotrichum gloeosporioides*, *Colletotrichum gossypii* var., *Colletotrichum lindemuthianum*, *Colletotrichum truncatum*, *Conoderus scalaris*, *Cornitermes bequaerti*, *Cornitermes cumulans*, *Corynespora cassiicola*, *Crysodeixis includens*, *Deois flavopicta*, *Deois lignosellus*, *Diabrotica speciosa*, *Diaporthe phaseolorum* var., *Dichelops melacanthus*, *Diloboderus abderus*, *Drechslera teres*, *Elasmopalpus lignosellus*, *Elsinoe ampelina*, *Elsinoe australis*, *Elsinoe fawcetti*, *Empoasca kraemeri*, *Enneothrips flavens*, *Epinotia aporema*, *Erysiphe diffusa*, *Euetheola humilis*, *Eutinobothrus brasiliensis*, *Frankliniella schultzei*, *Frankliniella williamsi*, *Fusarium graminearum*, *Fusarium moniliforme*, *Fusarium oxysporum* f.sp., *Fusarium pallidoroseum*, *Helicoverpa armigera*, *Heliothis virescens*, *Hemileia vastatrix*, *Heterotermes tenuis*, *Julus hesperus*, *Lasiodiplodia theobromae*, *Leandria momordicae*, *Meloidogyne incognita*, *Meloidogyne javanica*, *Metopolophium dirhodum*, *Microsphaera diffusa*, *Migdolus fryanus*, *Mycosphaerella fragariae*, *Mycosphaerella musicola*, *Neocapritermes opacus*, *Oidium* sp., *Oryzophagus oryzae*, *Penicillium* spp., *Phaeoisariopsis griseola*, *Phoma costaricensis*, *Phomopsis sojae*, *Phyllophaga cuyabana*, *Phyllophaga triticophaga*, *Phyllosticta citricarpa*, *Plasmopara viticola*, *Porcellio laevis*, *Pratylenchus brachyurus*, *Pratylenchus zaeae*, *Procornitermes triacifer*, *Pseudocercospora personata*, *Pseudoperonospora cubensis*, *Puccinia horiana*, *Puccinia psidii*, *Puccinia tritici*, *Pyricularia grisea*, *Ramularia areola*, *Rhizoctonia solani*, *Rhopalosiphum graminum*, *Rhopalosiphum maidis*, *Rhopalosiphum rufiabdominale*, *Sclerotinia sclerotiorum*, *Septoria glycines*, *Septoria lactucae*, *Septoria lycopersici*, *Septoria tritici*, *Sphaerotheca fuliginea*, *Sphaerotheca pannosa*, *Sphenophorus levis*, *Spodoptera eridania*, *Spodoptera frugiperda*, *Stagonospora nodorum*, *Sternechus subsignatus*, *Syntermes molestus*, *Thrips tabaci*, *Tranzschelia discolor*, *Uromyces alstroemeriae*, *Uromyces appendiculatus* and *Ceratocystis paradoxa*.

31. The method according to any of claims 16 to 30, wherein the plants being treated are selected from maize, rice, wheat, soybean, cotton and sugarcane.

5 32. Use in preventing, controlling and/or treating insecticidal, nematode and fungicidal infestations in plants of the components:

(A) an insecticidal component comprising:

(A1) fipronil; and

(A2) thiodicarb;

10 and

(B) a fungicidal component comprising:

(B1) azoxystrobin; and

(B2) carbendazim.

15 33. The use according to claim 32, wherein the weight ratio of component (A) to component (B) is from 50:1 to 1:50.

34. The use according to claim 33, wherein the weight ratio of component (A) to component (B) is from 1.1:1 to 50:1.

20 35. The use according to any of claims 32 to 34, wherein the weight ratio of fipronil to thiodicarb is from 15:1 to 1:15.

25 36. The use according to any of claims 32 to 35, wherein the weight ratio of azoxystrobin to carbendazim is from 20:1 to 1:20.

37. The use according to any of claims 32 to 36, wherein two or more of the components (A1), (A2), (B1) and (B2) are employed separately.

38. The use according to claim 37, wherein the components (A1), (A2), (B1) and (B2) are employed in two or more separate compositions.

5 39. The use according to any of claims 32 to 36, wherein the components (A1), (A2), (B1) and (B2) are employed simultaneously.

40. The use according to claim 39, wherein a single composition comprising components (A1), (A2), (B1) and (B2) is employed.

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41. The use according to claim 40, wherein the composition is formulated as a water-soluble concentrate (SL), an emulsifiable concentrate (EC), an emulsion (EW), a micro-emulsion (ME), a suspension concentrates (SC), an oil-based suspension concentrate (OD), a flowable suspension (FS), water-dispersible granules (WG), water-soluble granules (SG), a  
15 water-dispersible powder (WP), a water soluble powder (SP), granules (GR), encapsulated granules (CG), fine granules (FG), macrogranules (GG), an aqueous suspo-emulsion (SE), a microencapsulated suspension (CS), and microgranules (MG).

42. The use according to claim 41, wherein the composition is a suspension concentrate  
20 (SC) or a flowable suspension (FS).

43. The use according to any of claims 40 to 42, wherein a composition according to any of claims 1 to 15 is employed.

25 44. The use according to any of claims 32 to 43, wherein the components (A) and (B) are applied to the locus of the plants at a rate of from 0.1 to 4 kg/ha.

45. The use according to any of claims 32 to 44, wherein the components (A) and (B) are applied to the plant propagation material at a rate of from 10 to 700 g/100kg.

46. The use according to any of claims 32 to 45, wherein the species being controlled is one or more selected from *Alabama argillacea*, *Alternaria brassicae*, *Alternaria dauci*, *Alternaria porri*, *Alternaria solani*, *Anticarsia gemmatilis*, *Aphis gossypii*, *Aracanthus mourei*, *Aspergillus flavus*, *Aspergillus spp.*, *Asperisporium caricae*, *Atta capiguara*, *Bemisia tabaci*, *Bipolaris sorokiniana*, *Cercospora arachidicola*, *Cercospora beticola*, *Cercospora offeicola*, *Cercospora kikuchii*, *Cercospora soja*, *Cerotelium fici*, *Colletotrichum gloeosporioides*, *Colletotrichum gossypii* var., *Colletotrichum lindemuthianum*, *Colletotrichum truncatum*, *Conoderus scalaris*, *Cornitermes bequaerti*, *Cornitermes cumulans*, *Corynespora cassiicola*, *Crysodeixis includens*, *Deois flavopicta*, *Deois lignosellus*, *Diabrotica speciosa*, *Diaporthe phaseolorum* var., *Dichelops melacanthus*, *Diloboderus abderus*, *Drechslera teres*, *Elasmopalpus lignosellus*, *Elsinoe ampelina*, *Elsinoe australis*, *Elsinoe fawcetti*, *Empoasca kraemeri*, *Enneothrips flavens*, *Epinotia aporema*, *Erysiphe diffusa*, *Euetheola humilis*, *Eutinobothrus brasiliensis*, *Frankliniella schultzei*, *Frankliniella williamsi*, *Fusarium graminearum*, *Fusarium moniliforme*, *Fusarium oxysporum* f.sp., *Fusarium pallidoroseum*, *Helicoverpa armigera*, *Heliothis virescens*, *Hemileia vastatrix*, *Heterotermes tenuis*, *Julus hesperus*, *Lasiodiplodia theobromae*, *Leandria momordicae*, *Meloidogyne incognita*, *Meloidogyne javanica*, *Metopolophium dirhodum*, *Microsphaera diffusa*, *Migdolus fryanus*, *Mycosphaerella fragariae*, *Mycosphaerella musicola*, *Neocapritermes opacus*, *Oidium sp.*, *Oryzophagus oryzae*, *Penicillium spp.*, *Phaeoisariopsis griseola*, *Phoma costaricensis*, *Phomopsis sojae*, *Phyllophaga cuyabana*, *Phyllophaga triticophaga*, *Phyllosticta citricarpa*, *Plasmopara viticola*, *Porcellio laevis*, *Pratylenchus brachyurus*, *Pratylenchus zaei*, *Procornitermes triacifer*, *Pseudocercospora personata*, *Pseudoperonospora cubensis*, *Puccinia horiana*, *Puccinia psidii*, *Puccinia tritici*, *Pyricularia grisea*, *Ramularia areola*, *Rhizoctonia solani*, *Rhopalosiphum graminum*, *Rhopalosiphum maidis*, *Rhopalosiphum rufiabdominale*, *Sclerotinia sclerotiorum*, *Septoria glycines*, *Septoria lactucae*, *Septoria lycopersici*, *Septoria tritici*, *Sphaerotheca fuliginea*, *Sphaerotheca pannosa*, *sphenophorus levis*, *Spodoptera eridania*, *Spodoptera frugiperda*, *Stagonospora nodorum*, *Sternechus subsignatus*, *Syntermes molestus*, *Thrips tabaci*, *Tranzschelia discolor*, *Uromyces alstroemeriae*, *Uromyces appendiculatus* and *Ceratocystis paradoxa*.

47. The use according to any of claims 32 to 46, wherein the plants being treated are selected from maize, rice, wheat, soybean, cotton and sugarcane.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2019/130378

**A. CLASSIFICATION OF SUBJECT MATTER**

A01N 47/02(2006.01)i; A01N 47/18(2006.01)i; A01N 43/54(2006.01)i; A01N 47/24(2006.01)i; A01P 5/00(2006.01)i; A01P 7/04(2006.01)i; A01P 3/00(2006.01)i

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; A01P

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)

CNABS, DWPI, SIPOABS, CNKI, STN(CAPLUS): fipronil, thiodicarb, Azoxystrobin, strobilurins, carbendazim

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                          | Relevant to claim No. |
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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

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

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

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

“&” document member of the same patent family

Date of the actual completion of the international search

23 March 2020

Date of mailing of the international search report

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**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2019/130378**

| Patent document<br>cited in search report |           |   | Publication date<br>(day/month/year) | Patent family member(s) |              |    | Publication date<br>(day/month/year) |
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| CN                                        | 103843806 | A | 11 June 2014                         | None                    |              |    |                                      |
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