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(71) Applicant: **ROTAM AGROCHEM INTERNATIONAL COMPANY LIMITED** [CN/CN]; Unit 6, 26/f, Trend Centre, 29 Cheung Lee Street, Chai Wan, Hong Kong (CN).

(72) Inventor: **BRISTOW, James Timothy**; Unit 6, 26/F, Trend Centre, 29 Cheung Lee Street, Chai Wan, Hong Kong (CN).

(74) Agent: **SHANGHAI PATENT & TRADEMARK LAW OFFICE, LLC**; 435 Guiping Road, Shanghai 200233 (CN).

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(54) Title: SUBMICRON IMIDACLOPRID AND ABAMECTIN COMPOSITIONS

(57) Abstract: The present invention relates to novel suspension concentrate and suspoemulsion for formulations comprising imidacloprid and abamectin, having an average particle size of less than 1 micron.

SUBMICRON IMIDACLOPRID AND ABAMECTIN COMPOSITIONS

Technical field

The present invention relates to a suspension concentrate (SC) and suspoemulsion (SE) formulations comprising imidacloprid and abamectin, having an average particle size of less than 1 micron.

Background

Imidacloprid has an IUPAC name of (E)-1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine. Imidacloprid controls sucking insects, including rice, leaf and planthoppers, aphids, thrips and whiteflies. It is also effective against soil insects, termites and some biting insects, such as rice water weevil and Colorado beetle. Imidacloprid can be used as seed dressing, as soil treatment and as foliar treatment in different crops, *e.g.,* rice, cotton, cereals, maize, sugar beet, potatoes, vegetables, citrus fruit, pome fruit and stone fruit. It is generally commercialized as emulsion concentrate (EC), suspension concentrate (SC), soluble liquid (SL) and wettable powder (WP) formulations.

Abamectin is isolated from the fermentation of *Streptomyces avermitilis*, a naturally occurring soil actinomycete. Abamectin acts by stimulating the release of y-aminobutyric acid, an inhibitory neurotransmitter, thus finally activates chloride channels. Abamectin controls motile stages of mites, leaf miners, suckers, Colorado beetles, etc. on ornamentals, cotton, citrus fruit, pome fruit, nut crops, vegetables, potatoes and other crops. Abamectin is also used for controlling nematodes by seed treatment and fire ants. Abamectin is generally commercialized in EC formulation.

In recent years there has been a move towards increasing the efficacy, broaden the spectrum, and delay the resistance to insecticides by combining two or more active ingredients in the application.

CN1115964A describes a premix of imidacloprid and abamectin. It suggests the premix of imidacloprid and abamectin can be formulated as EC and WP.

US6,444,690B also describes a premix of imidacloprid and abamectin. It suggests that the mixture of the active ingredients can be formulated into customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols, active compound-impregnated natural and synthetic materials, very fine encapsulations in polymeric substances, and in coating formulations for seed, in formulations with smokes, such as fumigating cartridges, fumigating cans, fumigating coils and the like, and also ULV cold and warm mist formulation. These formulations are prepared in a known manner, for example by mixing the active ingredients with extenders (*e.g.,* liquid solvents, pressurized liquefied gases and/or solid carriers), optionally with surface-active agents, (e.g., emulsifying agents and/or dispersing agents, and/or foam-forming agents).

Generally, imidacloprid SL and abamectin EC with clear dilution have very good efficacy. However, substantial quantities of polar and non-polar organic solvents are required to provide a high efficacy of SL and EC formulations. Yet, these organic solvents are known for their toxicological and ecotoxicological properties, the use of organic solvents leading to corresponding problems. Therefore, the Institute for the Control of Agrochemicals, Ministry of Agriculture (ICAMA) has prohibited the registration of EC formulation. Further, although the EC formulation is not been banned in some countries, the standards of emulsion concentrates for obtaining registration have fundamentally been raised. Besides, it is difficult to formulate imidacloprid SL and abamectin EC without the use of the current solvent systems which contain polar and/or non-polar organic solvents. So, developing a premix of imidacloprid and abamectin to EC or SL faces formulation and concurrently regulatory problems.

Active ingredients are often administered in the form of aqueous systems. Water-based formulations are obtained by dissolving, emulsifying and/or suspending active ingredients in water. For the active ingredients having low water solubility, they would be difficult to formulate in the form of the aqueous system. The aqueous systems containing solid active ingredients may be formulated as suspension

concentrates (SC) or suspoemulsion (SE) formulations. However, these formulations are known to suffer from a variety of problems, such as agglomeration of solid active ingredients, irreversible thickening, serum formation or sedimentation as a hard packed precipitate. In the case of the SE formulation, the presence of an emulsified oil layer increases the risk of formulation failure due to the intrinsic instability of oil-in-water emulsions. Prolonged storage, storing at variation of extreme temperature, high-shearing and vibration increase the likelihood of failure.

The stability and efficacy of the current imidacloprid and abamectin SE or SC formulation are not good. As is known, generally the efficacy of SE and SC formulations is worse than the efficacy of EC and SL formulations.

Hence there is a need for improving the physical stability and efficacy of imidacloprid and abamectin SE or SC formulation.

The present invention provide a method to solve the physical stability and efficacy problems of imidacloprid and abamectin SE or SC formulation.

SUMMARY OF THE INVENTION

The present invention provides a method to prepare aqueous systems SE and SC formulations comprising imidacloprid and abamectin that exhibit improved physical storage stability, dispersibility, efficacy compared with a similar formulation having an average particle size in excess of 1 micron.

The present invention also relates to novel suspension concentrate (SC) and suspoemulsion (SE) formulations comprising imidacloprid and abamectin, one or both thereof having an average particle size of less than 1 micron.

The present invention further relates to an insecticide composition for controlling insects in crops, especially cotton, citrus, tomato, potato, green pepper, watermelon, coffee and soybean, by using the suspension concentrate and/or suspoemulsion formulations, and to a use of the formulations in controlling injurious insects in crops.

According to the present invention a suspension concentrate (SC) formulation is provided comprising imidacloprid and abamectin, one or both thereof having an average particle size of less than 1 micron and at least one dispersing agent.

The present invention further provides a suspoemulsion formulation comprising:

(A) a continuous aqueous phase;

(B) (i) a dispersed emulsion phase comprising at least one liquid and abamectin;

(ii) an emulsifier in a sufficient amount to emulsify the liquid and abamectin; and

(C) (i) a dispersed solid phase comprising imidacloprid having an average particle size of less than 1 micron;

(ii) at least one dispersing agent in a sufficient amount to disperse imidacloprid and any other solid technical material present in the formulation; wherein the solid phase is dispersed in aqueous and/or emulsion phase.

The invention also relates to a suspoemulsion formulation comprising:

(A) a continuous aqueous phase;

(B) (i) a dispersed emulsion phase comprising at least one liquid and imidacloprid;

(ii) an emulsifier in a sufficient amount to emulsify the liquid and imidacloprid; and

(C) (i) a dispersed solid phase comprising abamectin having an average particle size of less than 1 micron; and

(ii) a dispersing agent in a sufficient amount to disperse abamectin and any other solid technical material present in the formulation; wherein the solid phase is dispersed in aqueous phase and/or emulsion phase.

DETAILED DESCRIPTION OF THE INVENTION

Commercially available imidacloprid is formulated into soluble liquid (SL); and commercially available abamectin is normally formulated into emulsion concentrate (EC). Imidacloprid SL and abamectin EC are both known to exhibit a better biological efficacy. However, the use of organic solvents for preparing imidacloprid SL and abamectin EC is not good to the environment and the user. The aqueous systems/suspensions, like suspoemulsion (SE) and suspension concentrates (SC), do not have the problem occurring in EC or SL formulations. Recently, many kinds of SC have been developed. The aqueous systems/suspensions, however, are unavoidably inferior to the emulsifiable concentrate in biological effect. Particularly, when a water–insoluble active ingredient is used, the aqueous systems/suspensions are markedly inferior to the emulsifiable concentrate in biological effect.

SC formulation needs to apply at the dosage of 4 to 8 times more than EC one because the conventional SC formulation has a lower biological effect than EC formulation.

Therefore, the present invention provides aqueous systems/suspensions with improved biological effect by including the active ingredient(s) in form of fine particles. For this reason, the present invention provides a method to prepare pesticide formulations comprising imidacloprid and abamectin in which either or both active ingredients have a small particle size, i.e., less than 1 μm, to achieve a better biological effect as compared with a similar formulation having an average particle size in excess of 1 micron.

By providing the composition as disclosed herein also other problems associated with such compositions, such as agglomeration of solid particles, irreversible thickening, serum formation or sedimentation of solids as a hard packed precipitate have been found not to show up any more, so that the present pesticide formulations exhibit improved physical storage stability, dispersibility and efficacy as

compared with a similar formulation having an average particle size in excess of 1 micron.

The particle size of the active ingredient may be measured according to any technique known in the art, such as e.g. photoanalysis, sedimentation techniques, laser diffraction methods, acoustic spectroscopy or ultrasound attenuation spectroscopy etc.. Specifically, the particle size of the active ingredient may be measured by two different techniques, i.e. the Dv50 and Z-average. The Z-average diameter of the active ingredient as defined herein is measured by photon correlation spectroscopy using equipment readily determinable by those skilled in the art such as a Malvern Nanosizer. The Dv50 particle size of the active ingredient is the median particle size as determined using available analytical devices such as Malvern Mastersizer.

Preferably the phrase "having an average particle size of less than 1 micron" refers to the active ingredient having the average particle size as determined by both Dv50 and Z-average of below 1 micron. The results of Dv50 and Z-average will be similar, when the particle size distribution is narrow and below 1 micron. The results will not be similar when there is a significant fraction of particles larger than 1 micron.

The invention also relates to an aqueous suspension concentrate comprising imidacloprid and abamectin, one or both having an average particle size of less than 1 micron and at least one dispersing agent.

The invention also relates to a suspoemulsion formulation comprising:

(A) a continuous aqueous phase;

(B) (i) a dispersed emulsion phase comprising at least one liquid and abamectin;

(ii) an emulsifier in a sufficient amount to emulsify abamectin; and

(C) (i) a dispersed solid phase comprising imidacloprid having an average particle size of less than 1 micron;

(ii) a dispersing agent in a sufficient amount to disperse the imidacloprid

and any other solid technical material present in the formulation; wherein the solid phase is dispersed in the aqueous phase and/or emulsion phase.

Further, the invention relates to a suspoemulsion formulation comprising:

(A) a continuous aqueous phase;

(B) (i) a dispersed emulsion phase comprising at least one liquid and imidacloprid;

(ii) an emulsifier in a sufficient amount to emulsify the liquid and water-insoluble ingredients; and

(C) (i) a dispersed solid phase comprising abamectin having an average particle size of less than 1 micron;

(ii) a dispersing agent in a sufficient amount to disperse the abamectin and any other solid technical material present in the formulation; wherein the solid phase is dispersed in the aqueous phase and/or emulsion phase.

In some embodiments, imidacloprid has an average particle size of less than 1 micron as the dispersed solid phase in the suspoemulsion formulation. In certain embodiments, abamectin has an average particle size of less than 1 micron as the dispersed solid phase in the suspoemulsion formulation.

The amount of imidacloprid in the formulation may be in the range of from about 1% to about 80%, preferably from about 5% to about 70%, more preferably about 10% to about 60%, even more preferred from about 10% to about 50% or from about 15% to about 40%, more preferred about 30%. The amount of abamectin in the formulation may be in the range of from about 0.5% to about 80%, preferably from about 0.5% to about 70%, more preferably from about 1% to about 60% or from about 1% to about 50%, or from about 1% to about 40%, or even from about 1% to about 30%, even more preferred from about 1% to about 20% or from about 1% to about 10%).

In the suspensions, especially suspoemulsion, surfactants function as emulsifiers is use to emulsify the oil phase with one water-insoluble technical material

and dispersants to disperse another solid water-insoluble technical material. These surfactants should be compatible in one formulation. The surfactants may act as both an emulsifier and a dispersant.

Suitable surface-active compounds are, depending on the nature of the active ingredient, non-ionic, cationic and/or anionic surfactants and mixtures of surfactants having good emulsifying, dispersing and wetting properties.

Suitable anionic surfactants are known in the art. For example, poly-arylphenol polyalkoxyether sulfates and/or phosphates; C_{8-18} alcohol polyalkoxyether phosphates, carboxylates, and/or citrates; alkyl benzesulfonic acids; C_{8-20} alkyl carboyxlates including fatty acids; C_{8-20} alcohol sulfates; C_{8-20} alcohol phosphate mono-and diester; C_{8-20} alcohol and (C_{8-20} alkyl)phenol polyoxyethylene ether carboxylates, sulfates and sulfonates; C_{8-20} alcohol and (C_{8-20} alkyl)phenol poly-oxyethylene phosphate mono-and diesters; C_{8-20} alkylbenzene sulfonates, naphthalene sulfonates and formaldehyde concendates thereof; lignosulfonates; C_{8-20}-alkyl sulfosuccinates and sulfoccinamates; C_{8-20} acryl glutamates, sarcosinates, isethionates and taurates; water-soluble soaps and mixtures thereof. Commercially available polyarylphenol polyalkoxyether sulfates and phosphates include, for example, SOPROPHOR®4D384 (tristyrylphenol $(EO)_{16}$ sulfate ammonium salt, Rhodia Corporation), SOPROPHOR®3D33 (tristyrylphenol $(EO)_{16}$ phosphate free acid, Rhodia Corporation, SOPROPHOR®FLK (tristyrylphenol $(EO)_{16}$ phosphate potassium salt, Rhodia Corporation), SOPROPHOR®RAM/384 (tristyrylphenol polyethoxylated ether sulfate neutralized with polyethoxylated oleylamine, Rhodia Corporation). Commercially available C_{8-18} alcohol polyethoxyether phosphates, carboxylates and cetrates include STEPFAC® 8180 (tridecylalcohol $(EO)_3$ phosphate, Stepan Corporation), STEPFAC®8181 (tridecylalcohol $(EO)_6$ phosphate), Stepan Corporation), STEPFAC®8182 (tridecylalcohol $(EO)_{12}$ phosphate, Stepan Corporation). Exemplary alkylbenzene sulfonic acids and salts thereof include dodecylbenzene sulfonic acid, and metal (for example sodium or calcium), ammonia or amine salts of the alkylbenzene sulfonic acids, including dodecylbenzene sulfonic

acid. Amine neutralized versions include primary amines, diamines, triamines and alkanol amines.

Exemplary nonionic surfactants include ethylene oxide-propylene oxide block copolymers; ethylene oxide-butylene oxide block copolymers; C_{2-6} alkyl adducts of ethylene oxide-propylene oxide block copolymers; C_{2-6} alkyl adducts of ethylene oxide-butylene oxide block copolymer; polypropylene glycol; polyethylene glycols; polyarylphenol polyethoxy ethers; polyalkylphenol polyethoxy ethers; polyglycol ether derivatives of aliphatic or cycloaliphatic alcohols or of saturated or unsaturated fatty acids and alkylphenol. Commercially available nonionic surfactants include, for example, TOXIMUL®8320 (butyl ether derivative of EO/PO block copolymer, Stepan Corporation), WITCONOL®NS-500LQ (butyl ether derivative of EO/PO block copolymer, CK Witco Corporation).

Suitable non-ionic surfactants are nonlyphenol polyethoxy ethanols, vegetable oil polyglycol ethers, polyadducts of ethylene oxide and propylene oxide, tributyl phenoxy polyethoxy ethanol, octayl phenoxy polyethoxy ethanol.

Cation surfactants are preferably quaternary ammonium salts carrying, as N-substituted, at least one C_8-C_{22} alkyl radical and, as further substituents, unsubstituted or halogenated lower alkyl, benzyl or hydroxyl-lower alkyl radicals. The salts are preferably in the form of halides, methyl sulfates or ethyl sulfates, for example stearyl trimethylammonium chloride or benzyl bis(2-chloroethyl)ethyl-ammonium bromide.

The amount of surfactant(s) depends on the particular active ingredients selected for the composition and the absolute and relative amounts of these desired. Suitable amount of surfactants selected from the classes or specific examples provided herein can be determined by routine experimentation, the test being that substantially no phase separation, sedimentation or flocculation is exhibited by the composition following storage at 20 - 25 ^{o}C for a period of 24 hours, or, for preferred embodiments, following a longer period of storage over a broader range of temperatures as indicated above. Typically the total amount of surfactants in the

composition / formulation is ranged from about 1 % to about 30 % by weight of the composition / formulation. The surfactants may act as both an emulsifier and a dispersant. The amount of the emulsifier is ranged from about 1 % to about 30 % by weight of the composition / formulation. The amount of the dispersant is ranged from about 1 % to about 30 % by weight of the composition / formulation.

These compositions may also comprise other auxiliaries such as wetting agents, chemical stabilizers, viscosity controlling agents, thickeners, binders, tackifiers, fertilizers and anti-foam agents.

Examples of suitable polymeric stabilizers that may be used in the present invention have a molecular weight between 10,000 and 1,000,000 daltons and include, but are not limited to polypropylene, polyisobutylene, polyisoprene, copolymers of monoolefins and diolefins, polycarylates, polystyrene, polyvinyl acetate, polyurethanes or polyamides.

Representative anti-foam agents are silica, polydialkylsiloxanes, in particular polydimethylsiloxanes, fluoroaliphatic esters or perfluoroalkylphosphonic/perfluoro-alkylphosphonic acids or the salts thereof and mixtures thereof. Preferred are polydimethylsiloxanes.

The formulation in general comprise between 0.1 % and 95 % by weight of the composition, preferably between 0.5 % and 90 %.

The imidacloprid and abamectin mixtures are suitable for combating animal pest, in particular insects, arachnids and nematodes, encountered in agriculture, in forestry, in the protection of stored products and of materials, and in the hygiene filed, and have good plant tolerance and favorable toxicity to warm-blooded animals. They are active against normally sensitive and resistant species and against all or some stages of developments. The pests include aphids, citrus rustmite, whitefly, spider mite, russet mite and redbanded stink bug, etc.

The rates of application (use) of the composition of the present invention may vary widely. The rate at which the compositions are applied will depend upon the

particular type of insects to be controlled, the degree of control required, and the timing and method of application. In general, the compositions can be applied in an amount such that imidacloprid and abamectin at a rate of 10 - 400 g a.i. per ha, preferably 20 - 300 g a.i. per/ha.

The following examples are given by way of illustration and not by way of limitation of the invention. Where not otherwise specified throughout this specification and claims, percentages are by weight.

EXAMPLES

Example 1

	% wt
Imidacloprid	30
Abamectin	2.8
PLURONIC®PE 6800 (BASF)	3.5
TERSPERSE®2500 (Huntsman)	1.5
Silicone antifoam agent	0.1
Xanthan gum	0.2
Propylene glycol	5.0
Preservative	0.15
Water	balance to 100

1.1 Preparation of imidacloprid and abamectin mill base

The suitable amount water, non-ionic and ionic surfactants and imidacloprid and abamectin were mixed together. The antifoam agent and suitable amount xanthan gum were added and mixed until uniform. If needed, the millbase was milled to the desired particle size.

1.2 Preparation of final product

According to the above composition, propylene glycol, xanthan gum and preservative and water were added into the imidacloprid and abamectin millbase and blended until uniform.

Example 2

2.1 Preparation of abamectin EW

	Wt%
Abamectin	10
N-methyl pyrrolidone	20
TWEEN®80 (Croda)	5
RHODACAL®70B (Rhodia)	2
Water	22

Abamectin was dissolved in N-methyl pyrrolidone, then TWEEN®80and RHODACAL®70B were added and mixed until uniform to form an oil phase. The oil phase was then added to the water to form an emulsified oil phase with a particle size of 1-40 microns.

2.2 Preparation of imidacloprid millbase

	Wt %
Imidacloprid	60
PLURONIC®PE 6800 (BASF)	3.5
TERSPERSE®2500 (Huntsman)	1.5
Silicone antifoam agent	0.1
Xanthan gum	0.2
Water	54.7

Water, PLURONIC®PE 6800, TERSPERSE®2500 and imidacloprid were mixed together. The antifoam agent and xanthan gum were added and mixed until uniform. If needed, the millbase was milled to the desired particle size.

2.3 Preparation of final product

	Wt%
Abamectin EW	14
Imidacloprid millbase	50
Propylene glycol	5
TOXIMUL®8320 (Stepan)	6
Xanthan gum	0.15
Preservative	0.15
Water	balance to 100

The abamectin EW, propylene glycol, the TOXIMUL®8320 and some of the water were blended together. The imidacloprid millbase was added and blended. Next,

the xanthan gum and preservative were added and blended until uniform.

Example 3 sample preparation

3.1 Preparation of imidacloprid EW

	Wt%
Imidacloprid	60
N-methyl pyrrolidone	20
TWEEN®80 (Croda)	5
RHODACAL®70B	2
Water	balance to 100

Imidacloprid was dissolved in N-methyl pyrrolidone, then TWEEN®80 and RHODACAL®70B were added and mixed until uniform to form an oil phase. Then add the oil phase to the water to form an emulsified oil phase with a particle size of 1-40 microns.

3.2 Preparation of abamectin mill base

	Wt%
Abamectin	10
PLURONIC®PE 6800 (BASF)	3.5
TERSPERSE®2500 (Huntsman)	1.5
Silicone antifoam agent	0.1
Xanthan gum	0.2
Water	34.7

Water, PLURONIC®PE 6800, TERSPERSE®2500 and abamectin were mixed together. The antifoam agent and xanthan gum were added and mixed until uniform. If needed, the millbase was milled to the desired particle size.

2.3 Preparation of final product

	Wt%
Imidacloprid EW	50
Abamectin millbase	14
Propylene glycol	5
TOXIMUL®8320 (Stepan)	6
Xanthan gum	0.15
Preservative	0.15
Water	balance to 100

Imidacloprid EW, propylene glycol, TOXIMUL®8320 and water were blended

together. The abamectin millbase was added and blended. Next, the xanthan gum and preservative were added and blended until uniform.

Example 4

Re-dispersing of imidacloprid and/or abamectin millbase

Stability protocol: The millbase samples from section 1.1, 2.2, 3.2 were stored in 2 oz. jars at 38 °C for 6 weeks. The ability to re-disperse sediment was rated on how long, it takes to homogenize the sample by shaking at a moderate speed. Shorter time to re-disperse the sediment are desirable. The jars were shaken horizontally for two complete shake in one second (one complete shake = a complete forward and backward motion). The sediment must be completely re-dispersed, all sediment from the bottom of the jar and no lumps or agglomerates in the bulk of the sample.

Sample 1-1 represents a submicron millbase as set forth in section 1.1. Sample 2-1 represents a submicron mill base as set forth in section 2.2. Sample 3-1 represents a submicron mill base as set forth in section 3.2. Sample 1-2, 2-2, and 3-2 has a similar composition but contains millbase having larger particles.

Table 1

Sample	**Particle Size Malvern Nanovern Nanosizer* (Z-AVERAGE, μm)**	**Particle size Malvern Mastersizer* (Median, DV50, μm)**	**Time to Homogenize (second)**
1-1	0.621	0.58	25
1-2*	0.964	1.32	56
2-1	0.568	0.573	15
2-2*	1.212	1.523	80
3-1	0.854	0.892	10
3-2*	0.987	1.432	70

*Millbase outside the scope of the claimed invention

From Table 1, imidacloprid and/or abamectin having an average particle size

within the scope of the present invention (example 1-1, example 2-1 and example 3-1) were significantly easier to re-disperse.

Example 5

Improved dilution performance of final product with submicron millbase

Dilution protocol: The final product formulations from sections 1.2, 2.3 and 3.3, were diluted using water with a hardness of 50 ppm and 1000 ppm to 100 mL in 100 mL graduated cylinders. The graduated cylinders were inverted for 10 complete inversions. The cylinders were left undisturbed at room temperature for 24 hours. After 24 hours, the number of inversion needed to completely re-disperse the sediment was noted. The lower the number of inversion required to completely the sediment represents an improvement in the ability to re-disperse the final product.

Sample 2-1 represents a submicron millbase as described in section 1.2. Sample 3-1 represents a submicron millbase as described in section 2.3 Sample 4-1 represents a submicron millbase as described in section 3.3. Sample 2-2, sample 3-2 and sample 4-2 have a similar composition but contain millbase having a larger average particle size.

Table 2

Sample	**Final product / Millbase**	**50ppm**	**1000ppm**
2-1	Final product with submicron millbase	10 inversions	10 inversions
2-2*	Final product with non-submicron millbase	50 inversions	50 inversions
3-1	Final product with submicron millbase	6 inversions	6 inversions
3-2*	Final product with non-submicron millbase	30 inversions	30 inversion
4-1	Final product with submicron millbase	7 inversions	7 inversions
4-2*	Final product with non-submicron millbase	40 inversions	40 inversions

*Final product outside the scope of the claimed invention

It is clear from the data set forth in Table 2, that the final product formulation prepared from the imidacloprid and/or abamectin millbase having an average particle size within the scope of the present invention was significantly easier to re-disperse than the formulation containing the imidacloprid and/or abamectin millbase outside of the scope of the present invention as evidenced by the significantly fewer inversions required to homogenize the final product.

Example 6 - Efficacy Test

Efficacy test protocol: Final product formulation, as set forth in samples 1.2, 2.3 and 3.3, are prepared. Soybean leaves were treated by being dipped into the preparation of active ingredient of the desired concentration and have spider mites placed on them while the leaves are still moist. After 6 days, the kill in % is determined. 100% means that all the spider mites have been destroyed; 0% means that none of the spider mites has been destroyed.

Sample 2-1 represents a submicron millbase as described in section 1.2. Sample 3-1 represents a submicron millbase as described in section 2.3 Sample 4-1 represents a submicron millbase as described in section 3.3. Sample 2-2, sample 3-2 and sample 4-2 have a similar composition but contain millbase having a larger average particle size.

Table 3

Sample	**Final product / Millbase**	**Kill in % after 6 days (50 ppm)**	**Kill in % after 6 days (1000 ppm)**
2-1	Final product with submicron millbase	80	100
2-2*	Final product with non-submicron millbase	10	50
3-1	Final product with submicron millbase	90	100
3-2*	Final product with	30	60

	non-submicron millbase		
4-1	inal product with submicron millbase	90	100
4-2*	Final product with non-submicron millbase	40	70
Imidacloprid 200SL	Confidor, Bayer Crop)	70	80
Abamectin 1.8EC	Agrimec, Syngenta)	70	80
Imidacloprid 200SL + Abamectin 1.8EC	Tank mix	90	90

It is clear from the data set forth in Table 3, that the final product formulation prepared from the imidacloprid and/or abamectin millbase having an average particle size within the scope of the present invention exhibited a significantly higher efficacy than the formulation containing the imidacloprid and/or abamectin millbase outside of the scope of the present invention, the relevant emulsion concentrate formulation as evidenced by the significantly high insect-killing rate.

Although only a few exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this invention. Accordingly, all such modifications are intended to be included within the scope of this invention as defined in the following claims.

CLAIMS

1. A suspension concentrate or a suspoemulsion formulation comprising imidacloprid and abamectin, one or both thereof having an average particle size of less than 1 micron.

2. The suspension concentrate or suspoemulsion formulation according to claim 1, further comprising one or more of a dispersing agent and an emulsifier.

3. The suspension concentrate or suspoemulsion formulation according to claim 1 or 2, wherein the amount of imidacloprid in the formulation is in the range of from about 1% to about 80% and the amount of abamectin is in the range of from about 0.5% to about 80%.

4. The suspension suspoemulsion formulation according to any of claims 1-3, comprising:

(A) a continuous aqueous phase;

(B) (i) a dispersed emulsion phase comprising at least one liquid and abamectin;

(ii) an emulsifier in a sufficient amount to emulsify the liquid and abamectin; and

(C) (i) a dispersed solid phase comprising imidacloprid having an average particle size of less than 1 micron;

(ii) at least one dispersing agent in a sufficient amount to disperse imidacloprid and any other solid technical material present in the formulation; wherein the solid phase is dispersed in aqueous and/or emulsion phase.

5. The suspension suspoemulsion formulation according to any of claims 1-3, comprising:

(A) a continuous aqueous phase;

(B) (i) a dispersed emulsion phase comprising at least one liquid and imidacloprid;

(ii) an emulsifier in a sufficient amount to emulsify the liquid and imidacloprid; and

(C) (i) a dispersed solid phase comprising abamectin having an average particle size of less than 1 micron; and

(ii) a dispersing agent in a sufficient amount to disperse abamectin and any other solid technical material present in the formulation; wherein the solid phase is dispersed in aqueous phase and/or emulsion phase.

6. Use of a composition according to any of the preceding claims for controlling insects in crops.

7. The use according to claim 6, wherein the crops are selected from the group consisting of cotton, citrus, tomato, potato, green pepper, watermelon, coffee and soybean.

8. The use according to claim 6, wherein the insects are selected from the group consisting of rice-, leaf- and plant-hoppers, aphids, thrips and whiteflies, soil insects, termites, rice water weevil and Colorado beetle, mites, leaf miners, suckers, nematodes and fire ants.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2016/079367

A. CLASSIFICATION OF SUBJECT MATTER

A01N 25/04(2006.01)i; A01N 47/42(2006.01)i; A01N 43/90(2006.01)i; A01P 7/04(2006.01)n

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)

DWPI, CNABS, CNKI, SIPOABS: suspension, concentrate, suspoemulsion,formulation, imidacloprid, abamectin, particle w size, size, micron

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 101703066 A (GUANGXI TIANYUAN BIOCHEMISTRY) 12 May 2010 (2010-05-12) claim 1 and examples 2-3 in the description	1-8
Y	US 8563471 B2 (HOPKINSON MICHAEL ET AL.) 22 October 2013 (2013-10-22) claims 1-2, 5-6, 15-16, 24-25; column 1 line 40 to column 2 line 12; examples 1-3 in the description	1-8
Y	CN 1226382 A (ZHANG AEN) 25 August 1999 (1999-08-25) claims 1-2 and paragraphs 1-3 in the description	1-8
Y	CN 1985596 A (YUNNAN AGRICULTURAL UNIV) 27 June 2007 (2007-06-27) claim 1 and paragraph 1 in the description	1-8
Y	CN 104488947 A (XU GUAN AN) 08 April 2015 (2015-04-08) claim 1	1-8
Y	CN 1810117 A (SHI XIHONG) 02 August 2006 (2006-08-02) claim 1	1-8

☐ 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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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	Date of mailing of the international search report
24 June 2016	**06 July 2016**
Name and mailing address of the ISA/CN **STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China** Facsimile No. **(86-10)62019451**	Authorized officer **XU,Li** Telephone No. **(86-10)62084406**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2016/079367

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CN	104488947	A	08 April 2015	None			
CN	1810117	A	02 August 2006	None			