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(54) Title: SYSTEMIC BIOLOGICAL EFFICACY OF INSECTICIDES

(57) Abstract: Systemically active compositions comprising: A) at least one agrochemical formulation of an insecticide active ingredient, the melting point of the insecticide being greater than 75°C, and the water solubility of the insecticide being below 100 mg/L. B) at least one adjuvant formulation comprising B1. at least one adjuvant selected from the group of adjuvants b1-b4 wherein b1-b4 are selected from the groups comprising: b1. Vegetable oil esters, b2. Vegetable oil ethoxylates, b3. Vegetable oils, b4. White mineral oils, B2. at least one surfactant B3. optionally a liquid carrier B4. optionally further formulation components, and C) 82,000% to 99,973% by weight water, based on the total weight of the composition, wherein the weight ratio of the adjuvant to the insecticide in the composition is greater than 1.6.



Systemic Biological Efficacy of Insecticides

Insecticides can act by means of coming directly into contact with the pest to be controlled (contact activity), or by penetrating into the plant circulatory system (systemic activity/systemicity) and distributing themselves systemically in the plant. Thus, when the active acts systemically it comes into contact with the pest once the pest feeds on the plant. The systemic efficacy of insecticides is very advantageous because it allows the control of agrochemical pests without the need of a direct physical contact between the pest and the sprayed residue. This means that pest control can be achieved with systemic agrochemicals even when the sprayed residue has not reached the plant areas where the pest/fungi dwells: e.g. aphids localizing on the underside of leaves. In this way, systemicity can compensate for potentially suboptimal spraying conditions, and can ensure that all pests infecting the plant will be controlled as soon as the agrochemical has penetrated and distributed itself in the plant.

Therefore, it is advantageous to ensure that agrochemicals may act in a systemic manner. However, the physico-chemical properties necessary for a substance to act systemically are limited to a narrow band of log P (water / octanol distribution) and water solubility (*Pest Manag. Sci.* (2018), DOI 10.1002/ps.5037), and not all active ingredients which could potentially act systemically based on their mode of action are able to do so. Apart from sufficient water solubility to ensure solubilization in the plant circulatory system, a systemic agrochemical must also be able to penetrate through the plant cuticula, this being the main aerial physical barrier between the inner plant and the outside world.

Water-free formulations comprising a poorly water-soluble insecticide, a vegetable oil and a surfactant are known from WO2023/114120, WO2021/067678 and WO 2008/031512. US9,332,756 B2 discloses suspension concentrates containing cyantraniliprole, 40-55 wt. % methylated soybean oil, surfactants and up to 5 wt. % water. WO2023/114120 teaches that crystal growth in aqueous suspension concentrates containing indoxacarb and more than 50 wt. % water can be suppressed by using a combination of surfactant, polymeric dispersant and phosphate-based dispersant.

GABA gated chloride channel antagonists such as the fiproles are useful insecticides amongst other reasons because of their ability to exert a biological activity selectively against insects over vertebrates. This makes substances with this mode of action particularly useful, so that it would be advantageous to promote the systemic efficacy of fiproles. However, fiproles either have too little water solubility, or too high a log P, or both, and cannot act systemically (e.g. Ethiprole ~10 mg/L, logP ~3).

To the person knowledgeable in the art, it is known that some vegetable oils can increase the biological efficacy of fiproles: WO2003/028465 teaches that weight concentration ratios of oil/fiprole between 0.15 and 1.6 are necessary for increasing the biological efficacy of fiproles. However, this has only been shown for contact efficacy and not for systemic efficacy.

We have now found that the ratios and formulations taught in WO2003/028465 are not sufficient for inducing systemic activity of fiproles.

We have surprisingly found that fiproles can act systemically in the presence of specific adjuvants.

5 More particularly, we have found that white mineral oils, vegetable oils or vegetable oil derivatives when used in conjunction with fiproles will ensure that fiproles exert their insecticidal activity systemically against pests located on parts of the plant which have not been sprayed.

Hence, it is an object of the instant invention to provide fiprole comprising agrochemical formulations which have systemic activity when sprayed on plants, which still have good physical and chemical stability and good mixing properties.

10 This problem is solved by the formulations according to the instant invention as shown below.

The systemically active compositions according to the instant invention comprise:

- A) at least one agrochemical formulation of an insecticide active ingredient, the melting point of the insecticide being greater than 75°C, and the water solubility of the insecticide being below 100 mg/L,
- 15 B) at least one adjuvant formulation comprising
- B1. at least one adjuvant selected from the group of adjuvants b1-b4
- B2. at least one surfactant
- B3. optionally a liquid carrier
- B4. optionally further formulation components, and
- 20 C) 82,000% to 99,973% by weight water (carrier fluid), based on the total weight of the composition, wherein
- b1 – b4 are selected from the groups comprising:
- b1. Vegetable oil esters
- b2. Vegetable oil ethoxylates
- 25 b3. Vegetable oils
- b4. White mineral oils,

and wherein the weight ratio of the adjuvant to the insecticide in the composition is greater than 1.6.

Further, the compositions in a preferred embodiment are spray solutions to be used for the control of agronomically relevant pests.

Moreover, in ranges of preference stated in the present invention, the different levels of preference should be understood such that they can be combined with one another in permutations, but in any case identical levels of preference and especially the most preferred embodiment/level of preference in each case are to be combined with one another and are indeed disclosed as such a combination.

- 5 Compositions as described in the present application that consist solely of the essential components (not optional components) should likewise be considered to be disclosed.

Room temperature in the context of the present invention means, unless stated otherwise, a temperature of 20°C to 25°C.

Components A-C are defined further hereinafter.

10 A. Agrochemical formulation of an insecticide

The agrochemical formulation according to the invention may be provided to the end user in the form of concentrates which have to be diluted, preferably with water, prior to use. Agrochemical formulation types are known to the person knowledgeable in the art, and are disclosed in the CropLife International Technical Monograph number 2, 7th Edition (www.croplife.org)

- 15 (https://www.bvl.bund.de/DE/Arbeitsbereiche/04_Pflanzenschutzmittel/01_Aufgaben/08_Produktchemie/01_BeistoffeFormulierungschemie/01_Formulierungstypen/psm_BeistoffeFormulierungschemie_formulierungstypen_node.html).

Formulation Type

- 20 In a preferred embodiment of the invention, the formulation of an insecticide is chosen from the dispersion type formulations FS, SC, OD, or the solid type formulations WG, WP, SG.

More preferably, the formulation of an insecticide is selected from dispersion type formulations FS, SC, OD.

Further preferably, the formulation of an insecticide is selected from dispersion type formulations FS, SC.

Most preferably the formulation of an insecticide is selected from dispersion type formulations SC.

25 Formulation Loading

In a preferred embodiment of the invention, the agrochemical formulation carries a loading of active ingredient between 25-500 g/L.

In a more preferred embodiment of the invention, the agrochemical formulation carries a loading of active ingredient between 50-400 g/L.

In a further preferred embodiment of the invention, the agrochemical formulation carries a loading of active ingredient between 100-300 g/L.

In a most preferred embodiment of the invention, the agrochemical formulation carries a loading of active ingredient of 150 – 250 g/L.

5 Insecticide active ingredient

The insecticide present in the agrochemical formulation is preferably selected from insecticides known in the state of the art (“The Pesticide Manual; A World Compendium”; BCPC, 19th Edition), and whose melting point is greater than 75°C, and its water solubility lies below 100 mg/L.

10 More preferably the insecticide is selected from insecticides known in the state of the art (“The Pesticide Manual; A World Compendium”; BCPC, 19th Edition), and whose melting point is greater than 125°C, and its water solubility lies below 50 mg/L.

Further preferably the insecticide is selected from insecticides known in the state of the art (“The Pesticide Manual; A World Compendium”; BCPC, 19th Edition) and whose melting point is greater than 175°C, and its water solubility lies below 25 mg/L.

15 In an alternative embodiment of the invention the insecticide in the formulation is preferably selected from the IRAC Group 2, further preferably the insecticide in the formulation is selected from the IRAC Group 2B, most preferably the insecticide in the formulation is ethiprole.

In an alternative embodiment of the invention, the agrochemical formulation comprises a mixture of an insecticide in the IRAC Group 2 and an insecticide in the IRAC Group 4.

20 Examples of insecticides in the IRAC Group 2 are (Subgroup 2A) Chlordane, Endosulfan; (Subgroup 2B) Ethiprole, Fipronil

Examples of insecticides in the IRAC Group 4 are (Subgroup 4A) Acetamiprid, Clothianidin, Dinotefuran, Imidacloprid, Nitenpyram, Thiacloprid, Thiamethoxam; (Subgroup 4B) Nicotine; (Subgroup 4C) Sulfoxaflor; (Subgroup 4D) Flupyradifurone; (Subgroup 4E) Triflumezopyrim; (Subgroup 4F)
25 Flupyrimin.

In a preferred alternative embodiment of the invention, the agrochemical formulation comprises a mixture of an insecticide in the IRAC Group 2B and an insecticide in the IRAC Group 4A.

In a most preferred alternative embodiment of the invention, the agrochemical formulation comprises a mixture of ethiprole and imidacloprid.

30 In an alternative embodiment of the invention, the agrochemical formulation comprises a mixture of an insecticide in the IRAC Group 2 and an insecticide in the IRAC Group 3.

Examples of insecticides in the IRAC Group 3 are (Subgroup 3A) Acrinathrin, Allethrin, d-cis-trans Allethrin, d-trans Allethrin, Bifenthrin, Bioallethrin, Bioallethrin S-cyclopentenyl, Bioresmethrin, Cycloprothrin, Cyfluthrin, beta-Cyfluthrin, Cyhalothrin, lambda-Cyhalothrin, gamma-Cyhalothrin, Cypermethrin, alpha-Cypermethrin, beta-Cypermethrin, theta-Cypermethrin, zeta-Cypermethrin, Cyphenothrin [(1R)-trans- isomers], Deltamethrin, Empenthrin [(EZ)- (1R)- isomers], Esfenvalerate, Etofenprox, Fenpropathrin, Fenvalerate, Flucythrinate, Flumethrin, tau-Fluvalinate, Kadethrin, Pyrethrins (pyrethrum), Halfenprox, Phenothrin [(1R)-trans- isomer], Prallethrin, Resmethrin, Silafluofen, Tefluthrin, Tetramethrin, Tetramethrin [(1R)- isomers], Tralomethrin, Transfluthrin, Permethrin; (Subgroup 3B) DDT, Methoxychlor

10 In a preferred alternative embodiment of the invention, the agrochemical formulation comprises a mixture of an insecticide in the IRAC Group 2B and an insecticide in the IRAC Group 3A)

In a most preferred alternative embodiment of the invention, the agrochemical formulation comprises a mixture of ethiprole and beta-cyfluthrin.

Adjuvant formulation B)

15 The adjuvant formulation B) ensures a proper mixing and distribution of the adjuvant in the spray solution.

In the adjuvant formulation B further the at least one surfactant B2 is selected from the group comprising:

B2. at least one surfactant from the class which comprises

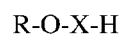
B2.1. Anionic surfactants selected from the group of

B2.1.1. alkyl substituted aryl sulfate and corresponding salts thereof, and

20 B2.1.2. alkyl substituted aryl phosphate and corresponding salts thereof.

B2.2. Non-ionic surfactants selected from the group of:

B2.2.1. linear or branched alcohol ethoxylate, according to Formula I,



(I)

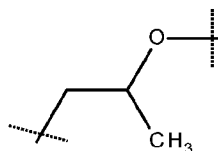
25 wherein R is a linear or branched C10-C18 alkyl radical, and X is a polyethylene glycol block, consisting of 4 to 15 ethylene oxide (formula III-b) units.

B2.2.2. block copolymer, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being represented as in Formula II.

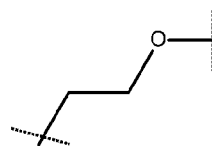
30 H-A-B-A-H

(II)

where B is a polypropylene glycol fragment consisting of 40 to 80 propylene oxide (PO) units (formula III-a) and A is a polyethylene glycol fragment consisting of 25 to 130 ethylene oxide (EO) units (formula III-b).



(III-a)



(III-b)

B3. optionally a liquid carrier

5 B4. optionally further formulation components.

Particle size and carrier C)

In an alternative embodiment the agrochemical formulation of an insecticide contains the insecticide as a finely milled solid in water, with particle sizes with d90 max. 20µm, further preferably with d90 max. 10µm, most preferably with d90 max 5µm.

10 In an alternative embodiment the agrochemical formulation of an insecticide contains the insecticide as a finely milled solid in water, with particle sizes with d50 max. 10µm, further preferably with d90 max. 5µm, most preferably with d90 max 2µm.

The composition according to the invention contains C) water as carrier fluid.

Components of the agrochemical formulation (B4)

15 Agrochemical formulations of insecticides according to the invention may contain additional or optional components (B4) needed to stabilize the dispersion of the active ingredient in the carrier. Such additives include dispersants, rheological modifiers, stabilizers (amongst others, antifoaming agents, antifreeze agents, pH adjusters, biocides).

Examples of dispersants

20 The dispersants can be an ionic (cationic or anionic), amphoteric or non-ionic surfactant, such as ionic or non-ionic or amphoteric dispersant(s), emulsifier(s), foam former(s), dispersant(s), wetting agent(s), and any mixtures thereof, including standard surface-active substances present in formulations of active agrochemical ingredients.

Examples of suitable anionic dispersants include, but are not limited to,

- salts of polyacrylic acid
- salts of polymers of mixtures of acrylic acid/acrylate esters
- salts of polymers of mixtures of acrylic acid/styrene
-
- 5 - salts of lignosulfonic acid (such as sodium lignosulfonate)
- salts of phenolsulfonic acid
- salts of condensation products of phenolsulphonic acid and formaldehyde
- salts of naphthalenesulfonic acid,
- salts of naphthalenesulphonic acid and formaldehyde condensation products
- 10 - salts of sulfonates of condensed naphthalenes or alkyl naphthalenes
- salts of sulfonates of dodecyl- and tridecylbenzenes
-
- salts of sulfosuccinic or sulfosuccinamate esters,
- salts of alkyl sulfates
- 15 - salts of alkyl polyethoxylated and/or polypropoxylated sulfates
- salts of paraffin sulfonates
- salts of alkyl sulfonates
- salts of alkyl polyethoxylated and/or polypropoxylated sulfonates
- salts of aryl sulfates
- 20 - salts of aryl polyethoxylated and/or polypropoxylated sulfates
- salts of aryl sulfonates
- salts of aryl polyethoxylated and/or polypropoxylated sulfonates
- salts of alkylaryl sulfates
- salts of alkylaryl polyethoxylated and/or polypropoxylated sulfates
- 25 - salts of alkylaryl sulfonates
- salts of alkylaryl polyethoxylated and/or polypropoxylated sulfonates
-
- salts of diphenyl sulfonates, and of diphenyloxide sulfonates
- salts of alpha-olefinsulfonates
- 30 - salts of sulfonates of fatty acids and oils
- salts of alpha-sulfonated methyl esters
- salts of taurine derivatives (preferably alkyl taurates)
- salts of isethionates
- 35 - salts of alkyl phosphoric esters
- salts of aryl phosphoric esters
- salts of alkylaryl phosphoric esters

- salts of phosphoric esters of polyethoxylated and/or polypropoxylated aliphatic linear or branched alcohols
 - salts of phosphoric esters of polyethoxylated and/or polypropoxylated aryl alcohols
- 5
- protein hydrolysates,
 - lignosulfite waste liquors
 - salts of polystyrenesulphonic acids
 - salts of polyvinylsulphonic acids
- 10
- salts of carboxylates
 - salts of ether carboxylates

Any reference to salts in this paragraph refers preferably to the respective alkali, alkaline earth and ammonium salts.

Examples of suitable cationic dispersants include, but are not limited to,

- 15
- those that contain units comprising primary, secondary, tertiary and/or quaternary amine groups that can either form part of the main polymer chain or can be borne by a side substituent directly connected thereto.
 - cationic polymers based on acrylamide, methacrylamide,
 - N-vinylpyrrolidone
- 20
- quaternized N,N-dimethylamino methacrylate,
 - diallyldimethylammonium chloride,
 - quaternized vinylimidazole (3-methyl-1-vinyl-1H-imidazol-3-ium chloride)
 - acrylamidopropyltrimonium chloride
 - cassia hydroxypropyltrimonium chloride,
- 25
- guar hydroxypropyltrimonium chloride or 25 polygalactomannan 2-hydroxypropyltrimethylammonium chloride ether
 - starch hydroxypropyltrimonium chloride and cellulose hydroxypropyltrimonium chloride.
 - polyquaternium-5, polyquaternium-6, polyquaternium-7, polyquaternium-10, polyquaternium-11, polyquaternium-16, polyquaternium-22, polyquaternium-28, polyquaternium-43,
- 30
- polyquaternium-44, polyquaternium-46

Examples of suitable non-ionic dispersants include, but are not limited to,

- polycondensates of ethylene oxide and propylene oxide
 - o compounds based on ethylene oxide and propylene oxide, having mean molar masses between 200 and 10 000 and preferably 1000 to 4000 g/mol, where the proportion by mass of the polyethoxylated block varies between 10% and 80%.
- 35

- polycondensates of ethylene oxide and/or propylene oxide with fatty alcohols
 - o polyethylene glycol ethers of branched or linear alcohols
 - o polypropylene glycol ethers of branched or linear alcohols
 - o polycondensates of polyethylene and polypropylene glycol ethers of branched or linear alcohols, whereby the polyethylene and polypropylene sections of the surfactant can be grafted next to each other, or they can be randomly interspersed.
 - o end group-capped and non-end group-capped alkoxyated linear and branched, saturated and unsaturated alcohols (e.g. butoxy polyethylene-polypropylene glycols),
 - polycondensates of ethylene oxide and/or propylene oxide with fatty acids
 - o reaction products of fatty acids or fatty acid alcohols with ethylene oxide and/or propylene oxide
 - polycondensates of ethylene oxide and/or propylene oxide with phenols, substituted phenols (preferably alkylphenols or arylphenols): such as tristyrylphenol ethoxylate or alkylaryl polyglycol ethers or nonylphenol ethoxylate
 - polycondensates of ethylene oxide and/or propylene oxide with fatty amines
 - polyoxyethylene fatty acid esters such as castor oil ethoxylate
 - polyoxyethylene fatty alcohol ethers
 - fatty esters of polyols (such as fatty acid esters of glycerol, sorbitol or sucrose), and ethoxylates thereof, such as esters of polyglycerin ethoxylates, or ester of ethoxylated sorbitol
 - fatty esters of alkanolamides
 - methylcellulose
 - polyvinyl alcohol
 - polyvinylpyrrolidone
 - o copolymer of PVP and dimethylaminoethyl methacrylate
 - o butylated PVP
 - copolymers of polyvinyl alcohol and polyvinylpyrrolidone
 - copolymers of (meth)acrylic acid and (meth)acrylic acid esters
 - polyoxyalkylenamines
 - polyoxyethylene alkanediol
 - polyoxyethylene and/or polyoxypropylene alkyne diols
 - copolymer of vinyl chloride and vinyl acetate and partially hydrolysed vinyl acetate
 - modified cellulose types
 - alkyl polyglucosides
- Examples of suitable amphoteric dispersants include, but are not restricted to
- Aminopropionates and iminodipropionates

- imidazoline derivatives, such as amphodiacetates, amphodipropionates, amphohydroxypropylsulfonates
- betaines
- sultaines
- 5 - phosphobetaines
- amine oxides

Preferred dispersants are selected from

- salts of phosphoric esters of polyethoxylated and/or polypropoxylated aryl alcohols

Preferred dispersants are more preferably selected from

- 10 - salts of phosphoric esters of polyethoxylated aryl alcohols

Preferred dispersants are further preferably selected from

- salts of phosphoric esters of polyethoxylated aryl alcohols containing 12-20 ethylene oxide units, wherein the general structure of the ethylene oxide unit is shown in (Formula III-b)

- Preferred dispersants can be described with the CAS Numbers 176776-21-9 (Poly(oxy-1,2-ethanediyl),
 15 .alpha.-tris(1-phenylethyl)phenyl-.omega.-hydroxy-, phosphate, potassium salt), or 163436-84-8 (Poly(oxy-1,2-ethanediyl),alpha-[2,4,6-tris(1-phenylethyl)phenyl]-.omega.-hydroxy-phosphate,potassium salt)

- Examples of salts of phosphoric esters of polyethoxylated and/or polypropoxylated aryl alcohols are
 DISPERSOGEN LFH, DISPERSOGEN TP 160, GERONOL CF/AR-E, LUCRAMUL PPS 16,
 20 LUCRAMUL PPS K 16, PHOSPHOLAN PHB 14, SOPROPHOR 3 D 33, SOPROPHOR FL, SOPROPHOR FL/60, SOPROPHOR FLK, SOPROPHOR TS 20-F, STEPFAK TSP PE-K, STEPFAK TSP-PE, SURFOM 1323 SC, SURFOM 1325 SC, TERSPERSE 2222.

- Examples of salts of phosphoric esters of polyethoxylated and/or polypropoxylated aryl alcohols are also
 dispersants with the CAS Numbers 39464-70-5 (Phenol ethoxylate phosphate ester), 90093-37-1 (2,4,6-
 25 Tris(1-phenylethyl)phenol polyoxyethylenated phosphates), 105362-40-1 (Polyethylene glycol 2,4,6-tristyrylphenyl ether phosphate triethanolamine salt), 163436-84-8 (Poly(oxy-1,2-ethanediyl), alpha.-2,4,6-tris(1-phenylethyl)phenyl-.omega.-hydroxy-, phosphate, potassium salt), 176776-21-9 (POLY(OXY-1,2-ETHANEDIYL), .ALPHA.-TRIS(1-PHENYLETHYL)PHENYL-.OMEGA.-HYDROXY-, PHOSPHATE, POTASSIUM SALT), 176776-21-9 (POLY(OXY-1,2-ETHANEDIYL),
 30 .ALPHA.-TRIS(1-PHENYLETHYL)PHENYL-.OMEGA.-HYDROXY-, PHOSPHATE, POTASSIUM SALT), 99734-09-5 (Poly(oxy-1,2-ethanediyl), ±-[2,4,6-tris(1-phenylethyl)phenyl]-É-hydroxy-, phosphate, potassium salt).

Examples of rheological modifiers

Suitable rheological modifiers by way of example are

- Polysaccharides including xanthan gum, guar gum and hydroxyethyl cellulose. Examples are Kelzan®, Rhodopol® G and 23, Satiaxane® CX911 and Natrosol® 250 range.
- 5 - Clays including smectite, montmorillonite, bentonite, sepiolite, attapulgit, laponite, hectorite. Examples are Veegum® R, Van Gel® B, Bentone® CT, HC, EW, Pangel® M100, M200, M300, S, M, W, Attagel® 50, Laponite® RD,
- Fumed and precipitated hydrophylic silica, examples are Aerosil® 200, Aerosil® 380, Sipernat® 22.
- 10 - Fumed and precipitated hydrophobic silica, examples are Aerosil® R812, Aerosil® R812S, Aerosil® R972

Preferred rheological modifiers are selected from

- Clays including smectite, montmorillonite, bentonite, sepiolite, attapulgit, laponite, hectorite. Examples are Veegum® R, Van Gel® B, Bentone® CT, HC, EW, Pangel® M100, M200, M300,
- 15 S, M, W, Attagel® 50, Laponite® RD.

Most particularly preferred rheological modifiers are selected from

- Smectite clays.

Most particularly preferred rheological modifiers are described by the CAS number 12199-37-0 (Smectite-group minerals)

20 Examples of stabilizers

Suitable stabilizers by way of example are

- Antifreeze, cold stabilizers, e.g. propylene glycol, ethylene glycol, urea, glycerine, inorganic salts (e.g. sodium chloride, potassium chloride, sodium sulfate, potassium sulfate.)
- preservatives, e.g. dichlorophene and benzyl alcohol hemiformal, 5-chloro-2-methyl-4-
- 25 isothiazolin-3-one [CAS-No. 26172-55-4], 2-methyl-4-isothiazolin-3-one [CAS-No. 2682-20-4] or 1,2-benzisothiazol-3(2H)-one [CAS-No. 2634-33-5]. Examples which may be mentioned are Preventol® D7 (Lanxess), Kathon® CG/ICP (Dow), Acticide® SPX (Thor GmbH) and Proxel® GXL (Arch Chemicals).
- antioxidants
- 30 - light stabilizers, in particular UV stabilizers,
- Butylhydroxytoluene [3,5-Di-tert-butyl-4-hydroxytoluol, CAS-No. 128-37-0]

Suitable antifoams by way of example are

- silicone antifoams and magnesium stearate,
- silicone oils, silicone oil preparations, particularly nonionic aqueous polydimethylsiloxane-based emulsions (dimethyl siloxanes and silicones, CAS No. 63148-62-9). Examples are Silcolapse® 482, 426 and 432 from Bluestar Silicones, Silfoam® SRE and SC132 from Wacker, SAG 1572 and SAG 30 from Momenive.

Suitable pH adjusters by way of example are

- acids and bases, such as, for example, hydrochloric acid, sulfuric acid, citric acid or sodium hydroxide and potassium hydroxide.
- buffers, e.g. suitable combinations of phosphate salts, or of citrate salts known in the literature to stabilize a concrete pH range.

Preparation of the agrochemical formulations

The agrochemical formulation according to the invention can be prepared in conventional manners, for example by mixing the compound combination of the invention with one or more suitable auxiliaries, such as disclosed herein above.

Formulation components are weighed in, homogenized with a high-shear device (e.g. Ultraturrax or colloidal mill) and subsequently milled in a bead mill until a particle size of $d_{90} < 20 \mu\text{m}$ is achieved.

Alternatively, formulation components are mixed in a bottle followed by addition of approx. 25vol.-% of 1.0-1.25 mm glass beads. The bottle is then closed, clamped in an agitator apparatus (e.g. Retsch MM301) and treated at 30 Hz for several minutes until a particle size of $d_{90} < 20 \mu\text{m}$ is achieved. After milling to the required particle size distribution, remaining components of the agrochemical formulation are mixed in to give a fine active substance suspension. The carrier is added in such an amount to result in a total amount of 100 % by weight.

B) Adjuvant Formulation

The adjuvant formulation B) preferably comprises :

1. at least one adjuvant selected from the group b1-b4
2. at least one surfactant
3. optionally a liquid carrier
4. optionally further formulation components, wherein

b1 - b4 are preferably selected from the group comprising

b1. Vegetable oil esters

b2. Vegetable oil ethoxylates

b3. Vegetable oils

b4. White Mineral oil

5 More preferred, b1 - b4 are preferably selected from the group comprising:

b1. Vegetable oil esters

b2. Vegetable oil ethoxylates

b3. Vegetable oils

Even more preferred b1 - b4 are preferably selected from the group comprising

10 b1. Vegetable oil esters

b2. Vegetable oil ethoxylates

Most preferred b1 - b4 are preferably selected from the group comprising

b1. Vegetable oil esters

15 In an alternative embodiment, the adjuvant b1 – b4 is selected from linear and/or branched alkyl esters of C10-C24 saturated and unsaturated fatty acids of vegetable or mineral origin: e.g. methyl, ethyl, propyl, butyl, pentyl, hexyl, isopropyl, isobutyl, isopentyl, 2-ethyl hexyl esters of capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, nonadecylic acid, arachidic acid, heneicosylic acid, behenic acid, tricosylic acid, lignoceric acid, α -Linolenic acid, linoleic acid, linolelaidic acid, palmitoleic acid, oleic acid, erucic acid.

20 In an alternative embodiment, the adjuvant b1 – b4 is most preferably selected from substances identified by the CAS Registry Number 68990-52-3 (C16-C18 fatty acid methyl esters).

In an alternative embodiment, the adjuvant b1 – b4 is preferably selected from the C1-C2 ester of sunflower oil, rapeseed oil, corn oil, soybean oil, rice bran oil, olive oil.

25 In an alternative embodiment, the adjuvant is b1 – b4 most preferably selected from rapeseed oil methyl ester and soybean oil methyl ester.

In an alternative / most preferred embodiment, the adjuvant b1 – b4 is soybean oil methyl ester.

Component B2: Surfactant

To ensure proper mixing and distribution of the adjuvant in the spray solution, it comprises a surfactant B2

As shown above, the at least one surfactant B2 is preferably selected from the group comprising:

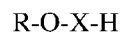
B2.1. Anionic surfactants in the form of

B2.1.1. alkyl substituted aryl sulfate and corresponding salts thereof, or

B2.1.2. alkyl substituted aryl phosphate and corresponding salts thereof.

5 B2.2. Non-ionic surfactant in the form of at least one of the classes which comprises

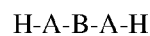
B2.2.1. linear or branched alcohol ethoxylate, as represented in Formula I,



(I)

10 Where R is a linear or branched C10-C18 alkyl radical, and X is a polyethylene glycol block, consisting of 4 to 15 ethylene oxide (formula III-b) units.

B2.2.2. block copolymer, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being represented as in Formula II.



15 (II)

where B is a polypropylene glycol fragment consisting of 40 to 80 propylene oxide (PO) units (formula III-a) and A is a polyethylene glycol fragment consisting of 25 to 130 ethylene oxide (EO) units (formula III-b).

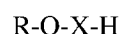
More preferably B2 is selected from the group comprising

20 B2.1. Anionic surfactants in the form of

B2.1.1. alkyl substituted aryl sulfate and corresponding salts thereof

B2.2. Non-ionic surfactant in the form of at least one of the classes which comprises

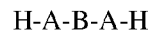
B2.2.1. linear or branched alcohol ethoxylate, as represented in Formula I,



25 (I)

Where R is a linear or branched C11-C17 alkyl radical, and X is a polyethylene glycol block, consisting of 5 to 14 ethylene oxide (formula III-b) units.

B2.2.2. block copolymer, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being represented as in Formula II.



5 (II)

where B is a polypropylene glycol fragment consisting of 45 to 75 propylene oxide (PO) units (formula III-a and A is a polyethylene glycol fragment consisting of 30 to 120 ethylene oxide (EO) units (formula III-b).

Even more preferred B2. is selected from the the group comprising

10 B2.1. Anionic surfactants in the form of

B2.1.1. Calcium dodecyl benzene sulfonate and corresponding salts thereof

B2.2. Non-ionic surfactant in the form of at least one of the classes which comprises

B2.2.1. linear or branched alcohol ethoxylate, as represented in Formula I,

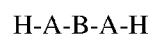


15 (I)

Where R is a linear or branched C12-C16 alkyl radical, and X is a polyethylene glycol block, consisting of 6 to 13 ethylene oxide (formula III-b) units

B2.2.2. block copolymer, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being represented as in Formula II.

20



(II)

where B is a polypropylene glycol fragment consisting of 50 to 70 propylene oxide (PO) units (formula III-a and A is a polyethylene glycol fragment consisting of 35 to 110 ethylene oxide (EO) units (formula III-b).

25

Examples of “**linear or branched alcohol ethoxylate**” are the product range “Genapol X” of Clariant, the product ranges “Lutensol AO”, “Lutensol TO” of BASF, the product range “Lucramul L” of Levaco

Examples of “**block copolymer**” are the product range “Pluronic PE” of BASF, or the product range “Synperonic PE” of Croda, or the product range Ultraric PE of Oxiteno.

In the context of the present invention, a linear C₁₀- to C₁₈-alkyl radical is understood to mean a decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl, heptadecanyl, octadecanyl radical.

5 In the context of the present invention, a branched C₁₀- to C₁₈-alkyl radical is understood to mean isomers of decanyl, undecanyl, dodecanyl, tridecanyl, tetradecanyl, pentadecanyl, hexadecanyl, heptadecanyl, octadecanyl radicals, whereby the carbon chain does not follow a linear configuration. In other words some of the carbon atoms are bound to 3 or 4 carbon atoms instead of each carbon atom in the chain being bound to only 2 carbon atoms.

10 B3. Optionally, the adjuvant formulation contains a liquid carrier preferably selected from the class which comprises water, organic solvents and combinations thereof.

In a further preferred embodiment component B3 is mandatory.

In a most preferred embodiment the adjuvant formulation contains water as liquid carrier B3.

Examples of suitable **liquid carriers** B3 include polar and nonpolar organic chemical liquids, for example from the classes of

- 15 - aromatic and nonaromatic hydrocarbons (such as cyclohexane, paraffins, alkylbenzenes, xylene, toluene, tetrahydronaphthalene, alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride),
- alcohols and polyols (which may optionally also be substituted, etherified and/or esterified, such as ethanol, propanol, butanol, benzylalcohol, cyclohexanol or glycol, 2-ethyl hexanol),
- 20 - ethers such as
 - o dioctyl ether, tetrahydrofuran, dimethyl isosorbide, solketal, cyclopentyl methyl ether, dibenzyl ether
 - o the Dowanol glycol ether products of Dow, or different grades of Polyethylene glycol ethers (e.g. Ethylene glycol monomethyl ether, Ethylene glycol monoethyl ether, Ethylene glycol monopropyl ether, Ethylene glycol monoisopropyl ether, Ethylene glycol monobutyl ether,
 - 25 Ethylene glycol monophenyl ether, Ethylene glycol monobenzyl ether, Diethylene glycol monomethyl ether, Diethylene glycol monoethyl ether, Diethylene glycol monopropyl ether, Diethylene glycol monoisopropyl ether, Diethylene glycol monobutyl ether, Diethylene glycol monophenyl ether, Diethylene glycol monobenzyl ether, Triethylene glycol monomethyl ether, Triethylene glycol monoethyl ether, Triethylene glycol monopropyl ether,
 - 30 Triethylene glycol monoisopropyl ether, Triethylene glycol monobutyl ether, Triethylene glycol monophenyl ether, Triethylene glycol monobenzyl ether),
 - o different grades of Polypropylene glycol ethers (e.g. Propylene glycol monomethyl ether, Propylene glycol monoethyl ether, Propylene glycol monopropyl ether, Propylene glycol monoisopropyl ether, Propylene glycol monobutyl ether, Propylene glycol monophenyl ether,
 - 35

- Propylene glycol monobenzyl ether, Dipropylene glycol monomethyl ether, Dipropylene glycol monoethyl ether, Dipropylene glycol monopropyl ether, Dipropylene glycol monoisopropyl ether, Dipropylene glycol monobutyl ether, Dipropylene glycol monophenyl ether, Dipropylene glycol monobenzyl ether, Tripropylene glycol monomethyl ether, Tripropylene glycol monoethyl ether, Tripropylene glycol monopropyl ether, Tripropylene glycol monoisopropyl ether, Tripropylene glycol monobutyl ether, Tripropylene glycol monophenyl ether, Tripropylene glycol monobenzyl ether)
- anisole, phenetole
 - different molecular weight grades of dimethyl polyethylene glycol, different molecular weight grades of dimethyl polypropylene glycol,
- ketones (such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclopentanone, cyclohexanone, cycloheptanone, acetophenone, propiophenone),
 - esters (also including methylated fats and oils such as rapeseed oil methyl ester, soybean oil methyl ester, coconut oil methyl ester, 2-ethyl hexyl palmitate, 2-ethyl hexyl stearate), such as butyl propionate, pentyl propionate, methyl hexanoate, methyl octanoate, methyl decanoate, 2-ethyl-hexyl acetate, benzyl acetate, cyclohexyl acetate, isobornyl acetate, benzyl benzoate, butyl benzoate, isopropyl benzoate,
 - di/triesters such as dimethyl succinate, dimethyl glutarate, dimethyl adipate, diisopropyl adipate, dibutyl adipate, Benzyl-2-ethylhexyl adipate, dimethyl 2-methyl glutarate, monoacetin, diacetin, triacetin, trimethyl citrate, triethyl citrate, triethyl acetyl citrate, tributyl citrate, tributyl acetyl citrate, as well as mixtures and blends thereof
 - lactate esters, such as methyl lactate, ethyl lactate, propyl lactate, butyl lactate, 2-ethyl hexyl lactate
 - (poly)ethers such as different molecular weight grades of polyethylene glycol, different molecular weight grades of polypropylene glycol
 - unsubstituted and substituted amines
 - amides (such as dimethylformamide, or N,N-dimethyl lactamide, or N-formyl morpholine, or fatty acid amides such N,N-dimethyl decanamide or N,N-dimethyl dec-9-en-amide) and esters thereof such as methyl 6-(dimethylamino)-2-methyl-6-oxo-hexanoate
 - lactams (such as 2-pyrrolidone, or N-alkylpyrrolidones, such as N-methylpyrrolidone, or N-butylpyrrolidone, or N-octylpyrrolidone, or N-dodecylpyrrolidone or N-methyl caprolactam, N-alkyl caprolactam)
 - lactones (such as gamma-butyrolactone, gamma-valerolactone, delta-valerolactone, or alpha-methyl gamma-butyrolactone
 - sulfones and sulfoxides (such as dimethyl sulfoxide),
 - nitriles, such as linear or cyclic alkyl nitriles, in particular acetonitrile, cyclohexane carbonitrile, octanonitrile, dodecanonitrile.
 - linear and cyclic carbonates, such as dimethyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate and isomers thereof, diphenyl carbonate, ethylene carbonate,

trimethylene carbonate, propylene carbonate, glycerol carbonate, butylene carbonate, pentylene carbonate, hexylene carbonate and octylene carbonate.

- phosphates, such as triethyl phosphate, tributyl phosphate, triisobutyl phosphate, trioctyl phosphate, tris(2-ethyl hexyl) phosphate
- 5 - mixtures of the any of the above such as,
 - ester mixtures such as Rhodiasolv RPDE,
 - mixtures of morpholine derivatives and cyclic carbonates such as Armid FMPC
 - mixtures of dimethyl sulfoxide with esters and/or with glycerine derivatives

B4. Optionally, the adjuvant formulation contains at least one further formulation components.

- 10 In a further preferred embodiment the at least one component B4 is mandatory.

As already indicated above, components B4 are preferably selected from the classes of

- Antifreeze, cold stabilizers, e.g. propylene glycol, ethylene glycol, urea, glycerine, inorganic salts (e.g. sodium chloride, potassium chloride, sodium sulfate, potassium sulfate.)
- preservatives, e.g. dichlorophene and benzyl alcohol hemiformal, 5-chloro-2-methyl-4-
15 isothiazolin-3-one [CAS-No. 26172-55-4], 2-methyl-4-isothiazolin-3-one [CAS-No. 2682-20-4] or 1.2-benzisothiazol-3(2H)-one [CAS-No. 2634-33-5]. Examples which may be mentioned are Preventol® D7 (Lanxess), Kathon® CG/ICP (Dow), Acticide® SPX (Thor GmbH) and Proxel® GXL (Arch Chemicals).
- antioxidants
- 20 - light stabilizers, in particular UV stabilizers,
- Butylhydroxytoluene [3.5-Di-tert-butyl-4-hydroxytoluol, CAS-No. 128-37-0]
- Antifoams. Suitable antifoams by way of example are
 - silicone antifoams and magnesium stearate,
 - silicone oils, silicone oil preparations, particularly nonionic aqueous
25 polydimethylsiloxane-based emulsions (dimethyl siloxanes and silicones, CAS No. 63148-62-9). Examples are Silcolapse® 426 and 432 from Bluestar Silicones, Silfoam® SRE and SC132 from Wacker, SAG 1572 and SAG 30 from Momentive.
- pH adjusters. Suitable pH adjusters by way of example are

- acids and bases, such as, for example, hydrochloric acid, sulfuric acid, citric acid or sodium hydroxide and potassium hydroxide. buffers, e.g. suitable combinations of phosphate salts, or of citrate salts known in the literature to stabilize a concrete pH range.

Formulation Type

- 5 In a preferred embodiment of the invention, the adjuvant formulation is chosen from formulations types in which the formulation is
- A liquid concentrate in which all components are dissolved, and which spontaneously emulsifies when mixed with water (self-emulsifiable concentrate).
 - An emulsion of the adjuvant in water.
- 10 In a most preferred embodiment of the invention, the adjuvant formulation is a liquid concentrate in which all components are dissolved, and which spontaneously emulsifies when mixed with water (self-emulsifiable formulation concentrate).

Formulation Loading

- In a preferred embodiment of the invention, the adjuvant formulation carries a loading of adjuvant between
- 15 18-94 % by weight.

In a more preferred embodiment of the invention, the adjuvant formulation carries a loading of adjuvant between 20-92 % by weight

In a most preferred embodiment of the invention, the adjuvant formulation carries a loading of adjuvant between 22-90 % by weight.

- 20 Preparation of the adjuvant formulation

The adjuvant formulation according to the invention can be prepared in conventional manners, for example by mixing the compound combination of the invention with one or more suitable auxiliaries, such as disclosed above.

Adjuvant formulation as self-emulsifiable concentrate

- 25 The components of the adjuvant formulation according to the invention are stirred until a homogeneous solution is obtained. Stirring can be done at any temperature between 20°C-60°C. Dilution with water gives an emulsion.

Adjuvant Formulation as emulsion in water

- Except for water, all other components of the adjuvant formulation according to the invention are stirred
- 30 until a homogeneous solution is obtained. This solution is added to the corresponding amount of water by

means of an emulsifying machine so as to obtain a homogeneous emulsion. The preparation of the emulsion can be done at any temperature between 20°C-60°C.

Compositions according to the invention

In a preferred embodiment, the invention provides an insecticidal composition comprising:

- 5 A as an FS, SC, OD, WG, WP, SG type formulation of an insecticide whose melting point is greater than 75°C, and its water solubility lies below 100 mg/L, and whose loading in the formulation lies between 25-500 g/L.

In an alternative embodiment a) is an FS, SC, OD, WG, WP, SG type formulation of an insecticide selected from the IRAC Group 2.

- 10 In an alternative embodiment of the invention, a) a mixture of an insecticide in the IRAC Group 2 and an insecticide in the IRAC Group 4.

In an alternative embodiment of the invention, a) a mixture of an insecticide in the IRAC Group 2 and an insecticide in the IRAC Group 3.

In a more preferred embodiment, the invention provides an insecticidal composition comprising:

- 15 A as an FS, SC, OD type formulation of an insecticide whose melting point is greater than 125°C, and its water solubility lies below 50 mg/L, and whose loading in the formulation lies between 50-400 g/L.

In an alternative embodiment A) is an FS, SC, OD type formulation of an insecticide selected from the fiprole group in IRAC Group 2B)

- 20 In an alternative embodiment of the invention, A) is an FS, SC, OD type formulation of a mixture of an insecticide in the IRAC Group 2B and an insecticide in the IRAC Group 4A)

In an alternative embodiment of the invention, A) is a mixture of an insecticide in the IRAC Group 2B and an insecticide in the IRAC Group 3A)

B. an adjuvant formulation comprising

B1. an adjuvant selected from

- 25 b1. Vegetable oil esters
 b2. Vegetable oil ethoxylates
 b3. Vegetable oils,

B2. at least one surfactant selected from the class which comprises

B2.1. Anionic surfactants in the form of

B2.1.1. alkyl substituted aryl sulfate and corresponding salts thereof

B2.2. Non-ionic surfactant in the form of at least one of the classes which comprises

B2.2.1. linear or branched alcohol ethoxylate, as represented in Formula I,

5 R-O-X-H

(I)

Where R is a linear or branched C11-C17 alkyl radical, and X is a polyethylene glycol block, consisting of 5 to 14 ethylene oxide (formula III-b) units.

10 B2.2.2. block copolymer, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being represented as in Formula II.

H-A-B-A-H

(II)

15 where B is a polypropylene glycol fragment consisting of 45 to 75 propylene oxide (PO) units (formula III-a and A is a polyethylene glycol fragment consisting of 30 to 120 ethylene oxide (EO) units (formula III-b),

B3. optionally a liquid carrier selected from the class which comprises water, organic solvents and combinations thereof, and

B4. optionally further formulation components.

20 C) water (carrier fluid).

In a further preferred embodiment, the invention provides an insecticidal composition comprising:

A) as an FS, SC type formulation of an insecticide whose melting point is greater than 175°C, and its water solubility lies below 25 mg/L, and whose loading in the formulation lies between 100-300 g/L.

25 In an alternative embodiment A) is an FS, SC type formulation of an insecticide selected from the fiprole group in IRAC Group 2B)

In an alternative embodiment of the invention, A) is an FS, SC type formulation of a mixture of an insecticide in the IRAC Group 2B and an insecticide in the IRAC Group 4A)

In an alternative embodiment of the invention, A) is an FS, SC type formulation of a mixture of an insecticide in the IRAC Group 2B and an insecticide in the IRAC Group 3A)

B. an adjuvant formulation comprising

B1. an adjuvant selected from

b1. Vegetable oil esters

b2. Vegetable oil ethoxylates

5 B2. at least one surfactant selected from the class which comprises

B2.1. Anionic surfactants in the form of

B2.1.1. alkyl substituted aryl sulfate and corresponding salts thereof

B2.2. Non-ionic surfactant in the form of at least one of the classes which comprises

B2.2.1. linear or branched alcohol ethoxylate, as represented in Formula I,

10
$$\text{R-O-X-H}$$

(I)

Where R is a linear or branched C11-C17 alkyl radical, and X is a polyethylene glycol block, consisting of 5 to 14 ethylene oxide (formula III-b) units.

15 B2.2.2. block copolymer, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being represented as in Formula II.

$$\text{H-A-B-A-H}$$

(II)

20 where B is a polypropylene glycol fragment consisting of 45 to 75 propylene oxide (PO) units (formula III-a) and A is a polyethylene glycol fragment consisting of 30 to 120 ethylene oxide (EO) units (formula III-b).

B3. optionally a liquid carrier selected from the class which comprises water, organic solvents and combinations thereof.

25 B4. optionally further formulation components.

C) water (carrier fluid).

In a most preferred embodiment, the invention provides an insecticidal composition comprising:

A) an SC type formulation of an insecticide whose melting point is greater than 175°C, and its water solubility lies below 25 mg/L, and whose loading in the formulation is 200 g/L.

In an alternative embodiment A) is an SC type formulation of ethiprole

- 5 In an alternative embodiment of the invention, A) is an FS, SC type formulation of a mixture of ethiprole and imidacloprid.

In an alternative embodiment of the invention, A) is an FS, SC type formulation of a mixture of ethiprole and beta-cyfluthrin.

B) an adjuvant formulation comprising

- 10 B1. An adjuvant selected from

b1. Vegetable oil esters

In an alternative embodiment the adjuvant is selected from rapeseed oil methyl ester, soybean oil methyl ester

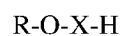
B2. At least one surfactant selected from the class which comprises

- 15 B2.1. Anionic surfactants in the form of

B2.1.1. Calcium dodecyl benzene sulfonate and corresponding salts thereof

B2.2. Non-ionic surfactant in the form of at least one of the classes which comprises

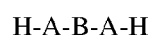
B2.2.1. linear or branched alcohol ethoxylate, as represented in Formula I,



- 20 (I)

Where R is a linear or branched C12-C16 alkyl radical, and X is a polyethylene glycol block, consisting of 6 to 13 ethylene oxide (formula III-b) units

B2.2.2. block copolymer, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being
25 represented as in Formula II.



(II)

where B is a polypropylene glycol fragment consisting of 50 to 70 propylene oxide (PO) units (formula III-a and A is a polyethylene glycol fragment consisting of 35 to 110 ethylene oxide (EO) units (formula III-b).

B3. Optionally a liquid carrier selected from the class which comprises water.

5 B4. Optionally further formulation components.

C) water (carrier fluid).

Concentrations of the ingredients in the compositions according to the invention

Percentages – unless stated otherwise – should be regarded as percentages by weight, where the % by weight of the compositions add up to 100.

10 The proportions of the individual components which follow are each based on the total weight of the composition, where the proportion up to 100% of the overall composition is made up by component C) (water). The proportion of component C) is 82,000% to 99,973% by weight, preferably of 93,833-98,930% by weight, more preferably of 97.000-99.850% by weight, most preferably of 98.000-99.825 % by weight, and even most preferably 98.400-99.900 by weight, based on the total weight of the composition.

15 The proportion of the agrochemical formulation (component A) in the compositions according to the invention is

preferably 0.007-16.000% by weight,

more preferably 0.020-4.667% by weight, and

further preferably 0.100-1.500% by weight,

20 most preferred 0.100 –0.750% by weight,

and even most preferred 0.120-0.500% by weight.

In an alternative embodiment the proportion of component A) in the composition according to the invention is determined by the concentration of active ingredient in the formulation. As such, the proportion of component A) present in the composition according to the invention is

25 preferably 0.007-16.000 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.0002-8.000% by weight, when the loading of the active ingredient in the formulation is 25 g/L – 500 g/L.

more preferably 0.020-4.667 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.001-1.867% by weight, when the loading of the active ingredient in the formulation is 50 g/L – 400 g/L.

5 further preferably 0.100-1.500 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.010-0.450% by weight, when the loading of the active ingredient in the formulation is 100 g/L – 300 g/L.

most preferably 0.100-0.750 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.020-0.150% by weight, when the loading of the active ingredient in the formulation is 200 g/L.

10 even most preferably 0.120-0.500 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.024-0.100% by weight, when the loading of the active ingredient in the formulation is 200 g/L.

In an alternative embodiment the proportion of component A) in the composition according to the invention is determined by the concentration of active ingredient in the formulation and the volume of water (component C) used per hectare. As such, the proportion of component A) present in the composition according to the invention is

15

preferably 0.007-16.000 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.0002-8.000% by weight, when the loading of the active ingredient in the formulation is 25 g/L – 500 g/L, and the volume of water (component C) used per hectare is 100-600 L/ha.

20 more preferably 0.020-4.667 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.001-1.867% by weight, when the loading of the active ingredient in the formulation is 50 g/L – 400 g/L and the volume of water (component C) used per hectare is 150-500 L/ha.

further preferably 0.100-1.500 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.010-0.450% by weight, when the loading of the active ingredient in the formulation is 100 g/L – 300 g/L and the volume of water (component C) used per hectare is 200-400 L/ha.

25

most preferably 0.100-0.750 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.020-0.150% by weight, when the loading of the active ingredient in the formulation is 200 g/L and the volume of water (component C) used per hectare is 200-400 L/ha.

30 even most preferably 0.120-0.500 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.024-0.100% by weight, when the loading of the active ingredient in the formulation is 200 g/L and the volume of water (component C) used per hectare is 200-400 L/ha.

In an alternative embodiment the proportion of component a) in the composition according to the invention is determined by the application rate of the active ingredient per hectare, the concentration of active ingredient in the formulation and the volume of water (component C) used per hectare. As such, the proportion of the formulated active ingredient present in the composition according to the invention is

5 preferably 0.007-16.000 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.0002-8.000% by weight, when the application rate of the active ingredient per hectare is 20 - 400 g/ha, and the loading of the active ingredient in the formulation is 25 g/L – 500 g/L, and the volume of water (component C) used per hectare is 100-600 L/ha.

10 more preferably 0.020-4.667 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.001-1.867% by weight, when the application rate of the active ingredient per hectare is 40 - 350 g/ha, when the loading of the active ingredient in the formulation is 50 g/L – 400 g/L and the volume of water (component C) used per hectare is 150-500 L/ha.

15 further preferably 0.100-1.500 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.010-0.450% by weight, when the application rate of the active ingredient per hectare is 60 - 300 g/ha, when the loading of the active ingredient in the formulation is 100 g/L – 300 g/L and the volume of water (component C) used per hectare is 200-400 L/ha.

20 most preferably 0.100-0.750 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.020-0.150% by weight, when the application rate of the active ingredient per hectare is 60 - 300 g/ha, when the loading of the active ingredient in the formulation is 200 g/L and the volume of water (component C) used per hectare is 200-400 L/ha.

even most preferably 0.120-0.500 % by weight which corresponds to a proportion of the corresponding formulated active ingredient of 0.024-0.100% by weight, when the application rate of the active ingredient per hectare is 60 - 300 g/ha, when the loading of the active ingredient in the formulation is 200 g/L and the volume of water (component C) used per hectare is 200-400 L/ha.

25 The proportion of the adjuvant formulation (component B) in the compositions according to the invention is

preferably 0.020-2.000 % by weight,

more preferably 0.050-1.500 % by weight,

most preferably 0.075-1.250 % by weight

30 even most preferably 0.090-1.100% by weight.

In an alternative embodiment the proportion of component B) in the composition according to the invention is determined by the concentration of adjuvant in the formulation. As such, the proportion of component b) present in the composition according to the invention is

preferably 0.020-2.000 % by weight which corresponds to a proportion of the corresponding adjuvant of
5 0.0036-1.880% by weight, when the loading of the adjuvant in the formulation is 18 – 94 %w/w.

more preferably 0.050-1.500 % by weight which corresponds to a proportion of the corresponding adjuvant of 0.010-1.380 % by weight, when the loading of the adjuvant in the formulation is 20 – 92 %w/w.

most preferably 0.075-1.250 % by weight which corresponds to a proportion of the corresponding adjuvant
10 of 0.016-1.125 % by weight, when the loading of the adjuvant in the formulation is 22 – 90 %w/w.

even most preferably 0.090-1.100 % by weight which corresponds to a proportion of the corresponding adjuvant of 0.0198-0.990 % by weight, when the loading of the adjuvant in the formulation is 22 – 90 %w/w.

In an alternative embodiment the proportion of component b) in the composition according to the
15 invention is determined by the concentration of adjuvant in the formulation and the volume of water (component C) used per hectare. As such, the proportion of component b) present in the composition according to the invention is

preferably 0.020-2.000 % by weight which corresponds to a proportion of the corresponding adjuvant of 0.0036-1.880% by weight, when the loading of the adjuvant in the formulation is 18 – 94 %w/w, and the
20 volume of water (component C) used per hectare is 100-600 L/ha.

more preferably 0.050-1.500 % by weight which corresponds to a proportion of the corresponding adjuvant of 0.010-1.380 % by weight, when the loading of the adjuvant in the formulation is 20 – 92 %w/w, and the volume of water (component C) used per hectare is 150-500 L/ha

most preferably 0.075-1.250 % by weight which corresponds to a proportion of the corresponding adjuvant
25 of 0.016-1.125 % by weight, when the loading of the adjuvant in the formulation is 22 – 90 %w/w and the volume of water (component C) used per hectare is 200-400 L/ha.

even most preferably 0.090-1.100 % by weight which corresponds to a proportion of the corresponding adjuvant of 0.0198-0.990 % by weight, when the loading of the adjuvant in the formulation is 22 – 90 %w/w and the volume of water (component C) used per hectare is 200-400 L/ha.

30 In an alternative embodiment, the composition of the components of component B) in the composition according to the invention are , preferably, when the proportion of B) in the composition according to the

invention is 0.020-2.000 % by weight, then Adjuvant b1-b4 is 0.0036-1.880% by weight Surfactant or mixture of surfactants is 0,00002-0.600% by weight,

more preferably, when the proportion of B) in the composition according to the invention is 0.050-1.500 % by weight, then Adjuvant b1-b4 is 0.010-1.380 % by weight, Surfactant or mixture of surfactants is
5 0,001-0.375% by weight

even more preferably, when the proportion of B) in the composition according to the invention is 0.075-1.250 % by weight, then Adjuvant b1-b4 is 0.016-1.125% by weight Surfactant or mixture of surfactants is 0,002-0.250% by weight,

even most preferably, when the proportion of B) in the composition according to the invention is 0.090-1.100 % by weight, then Adjuvant b1-b4 is 0.0198-0.990% by weight Surfactant or mixture of
10 surfactants is 0,0027-0.220% by weight.

A preferred embodiment of the invention is compositions comprising components

A) 0.007-16.000% by weight

B) 0.020-2.000 % by weight

15 C) to 100%, or 82,000% to 99,973% by weight.

A more preferred embodiment of the invention is compositions comprising components

A) 0.020-4.667% by weight

B) 0.050-1.500 % by weight

C) to 100%, or 93,833-98,930% by weight

20 A further-preferred embodiment of the invention is compositions comprising components

A) 0.100-1.500% by weight

B) 0.050-1.500 % by weight

C) to 100%, or 97.000-99.850% by weight

A most preferred embodiment of the invention is compositions comprising components

25 A) 0.100 –0.750% by weight

B) 0.075-1.250% by weight

C) to 100%, or 98.000-99.825% by weight.

An even most preferred embodiment of the invention is compositions comprising components

A) 0.120 – 0.500% by weight

B) 0.090-1.100% by weight

5 C) to 100%, or 98.400-99.790 by weight.

Alternative embodiment (concentration of AI in formulation/concentration of adjuvant in adjuvant formulation/volume of water):

In a preferred embodiment of the invention when the concentration of active ingredient in the agrochemical formulation A) is 25 g/L – 500 g/L, when the application rate of the active ingredient per
10 hectare is 20 - 400 g/ha, when the concentration of adjuvant in the adjuvant formulation B) is 18 – 94 % w/w, and when the volume of water C) is 100-600 L/ha, the compositions comprise components

A) 0.007-16.000% by weight, so that the proportion of the corresponding formulated active ingredient is 0.0002-8.000% by weight

B) 0.020-2.000 % by weight, so that the proportion of the corresponding formulated adjuvant is
15 0.0036-1.880% by weight.

C) to 100%, or 82,000% to 99,973% by weight.

In a more preferred embodiment of the invention when the concentration of active ingredient in the agrochemical formulation a) is 50 g/L – 400 g/L, when the application rate of the active ingredient per
20 hectare is 40 - 350 g/ha, when the concentration of adjuvant in the adjuvant formulation b) is 20 – 92 % w/w, and when the volume of water c) is 150-500 L/ha the compositions comprise components

A) 0.020-4.667% by weight, so that the proportion of the corresponding formulated active ingredient is 0.001-1.867% by weight

B) 0.050-1.500 % by weight, so that the proportion of the corresponding formulated adjuvant is 0.010-1.380 % by weight.

25 C) to 100%, or 93,833-98,930% by weight

In a further preferred embodiment of the invention when the concentration of active ingredient in the agrochemical formulation A) is 100 g/L – 300 g/L, when the application rate of the active ingredient per hectare is 60 - 300 g/ha, when the concentration of adjuvant in the adjuvant formulation B) is 20 – 92 % w/w, and when the volume of water C) is 200-400 L/ha the compositions comprise components

A) 0.100-1.500% by weight, so that the proportion of the corresponding formulated active ingredient is 0.010-0.450% by weight

B) 0.050-1.500 % by weight, so that the proportion of the corresponding formulated adjuvant is 0.010-1.380 % by weight.

5 C) to 100%, or 97.000-99.850%

In a an even more preferred embodiment of the invention when the concentration of active ingredient in the agrochemical formulation A) is 200 g/L, when the application rate of the active ingredient per hectare is 60 - 300 g/ha, when the concentration of adjuvant in the adjuvant formulation B) is 22 – 90 % w/w, and when the water C) is 200-400 L/ha the compositions comprise components

10 A) 0.100-0.750% by weight, so that the proportion of the corresponding formulated active ingredient is 0.020-0.150% by weight

B) 0.075-1.250% by weight, so that the proportion of the corresponding formulated adjuvant is 0.016-1.125 % by weight.

C) to 100%, or 98.000-99.825% by weight.

15 In an most preferred embodiment of the invention when the concentration of active ingredient in the agrochemical formulation A) is 200 g/L, when the application rate of the active ingredient per hectare is 60 - 300 g/ha, when the concentration of adjuvant in the adjuvant formulation B) is 22 – 90 % w/w, and when the volume of water C) is 200-400 L/ha are compositions comprising components

20 A) 0.120-0.500% by weight, so that the proportion of the corresponding formulated active ingredient is 0.024-0.100% by weight

B) 0.090-1.100% by weight, so that the proportion of the corresponding formulated adjuvant is 0.0198-0.990% by weight.

C) to 100%, or 98.400-99.790% by weight.

25 According to the invention, the weight ratio of the adjuvant to the insecticide in the composition, preferably spray solution, is greater than 1.6.

Preferably, the weight ratio of the adjuvant/insecticide in the composition, preferably spray solution, is greater than 2.0.

Most preferably the weight ratio of the adjuvant/insecticide concentration in the composition, preferably spray solution, is 2.3 or greater.

In each case, the weight ratio refers to the weight ratio of the insecticide alone without its formulation to the adjuvant alone without its formulation.

Applications of the formulations according to the invention

5 The application rate of the mixtures according to the invention can be varied within a relatively wide range. It is guided by the respective active ingredients in the agrochemical formulation a) and by the content of active ingredient thereof in the compositions in the agrochemical formulation a). The application volume of the compositions according to the invention can also be varied in a relatively wide range, which means that the applicable spray volume of water (carrier fluid) can be varied from 10 to 600 l/ha.

10 With the aid of the compositions according to the invention, the insecticidal active ingredient mixtures can be deployed in a particularly advantageous manner on plants and/or their habitat.

The compositions according to the invention can be used to treat all plants and parts of plants. Plants in this context are understood to include all plants and plant populations, such as desired and unwanted wild plants or crop plants (including naturally occurring crop plants). Crop plants may be plants which can be
15 obtained by conventional breeding and optimization methods or by biotechnological and genetic engineering methods or combinations of these methods, including the transgenic plants and including the plant cultivars which are protectable or non-protectable by plant breeders' rights. Parts of plants shall be understood to mean all parts and organs of the plants above and below ground, such as shoot, leaf, flower and root, examples given being leaves, needles, stalks, stems, flowers, fruit bodies, fruits and seeds, and
20 also tubers, roots and rhizomes. Plant parts also include harvested material and vegetative and generative propagation material, for example cuttings, tubers, rhizomes, shoots and seeds.

Preferably, the formulations according to the invention are used by spray application against animal pests from the following pest families:

Preference is given from the family of Aphididae to: Aphis sp. in cotton, soybean and vegetables

25 Preference is given from the family Curculionidae: Anthonomus sp. in cotton and Hypothenemus sp in coffee

Preference is given from the family Cercopidae to: Mahanarva sp. in crops such as sugar cane

Preference is given from the family Pentatomidae: Dichelops sp., Nezara sp., Piezodorus sp., Euschistus sp in soybean, corn and sorghum.

30 Preference is given from the family Cicadellidae to: Dalbulus sp. in corn

Preference is given from the family Thripidae to: Frankliniella sp., Thrips sp, Scirtothrips sp. in cotton, soybean and vegetables

Preference is given from the family Aleyrodidae to: Bemisia sp. in cotton, soybean and vegetables

Preference is given from the family Tetranychidae to: Tetranychus sp. in corn, soybean, cotton and
5 vegetables.

The inventive treatment of the plants and parts of plants with the compositions according to the invention is effected directly or by allowing the compositions to act on their surroundings, environment or storage space by the customary treatment methods, for example by drenching, immersion, spraying, evaporation, fogging, scattering, painting on.

10 Preferably, the plant to be treated is selected from the group consisting of cotton, soybean, corn, coffee, sugar cane, sorghum, vegetables

Preferably, the composition according to the invention acts against pests from the families of Aphididae, Curculionidae, Cercopidae, Pentatomidae, Cicadellidae, Thripidae, Aleyrodidae, Tetranychidae .

It has also been found that the compositions according to the invention can be produced by a process
15 having the steps of:

1) mixing ingredients (a) to (c) with subsequent homogenization. Relevant equipment for homogenization is known to those skilled in the art.

This process too forms part of the subject-matter of the invention.

Finally, it has been found that the compositions according to the invention are of very good suitability for
20 application of the active agrochemical ingredients present to plants and/or the habitat thereof. This process too forms part of the subject-matter of the invention. The examples which follow illustrate the subject-matter of the invention without limiting it.

Test and Methods used in the examples

Methods

25 Particle Size Measurement

The particle size is determined according to CIPAC (CIPAC = Collaborative International Pesticides Analytical Council; www.cipac.org) method MT 187. The particle size distribution is determined by means of laser diffraction. A representative amount of sample is dispersed in degassed water at ambient temperature (self-saturation of the sample), treated with ultrasound (usually 60 s) and then measured in a
30 device from the Malvern Mastersizer series (Malvern Panalytical). The scattered light is measured at

various angles using a multi-element detector and the associated numerical values are recorded. With the help of the Fraunhofer model, the proportion of certain size classes is calculated from the scatter data and from this a volume-weighted particle size distribution is calculated. Usually the d50 or d90 value = active ingredient particle size (50 or 90% of all volume particles) is given. The average particle size denotes the d50 value.

Alternatively, an optical microscope (40x magnification) may also be used to estimate the particle size.

Water Solubility

Water solubility is measured by saturating demineralized water with the solid to be analyzed. Water is kept at room temperature during the saturation process (20-22°C). After 12-24 hours the insoluble fraction is filtered and the concentration of substance to be analysed is measured in the filtrate using a suitable technique like HPLC, GC-MS.

Preparation of agrochemical formulation

Methods for the preparation of agrochemical formulations are well known to the expert in the art. Some examples of how to prepare these are shown below:

- 1) Formulation components are homogenized with a colloidal mill, and subsequently, milled in a bead mill (Dispermat SL50, 80% 2 mm beads, 4000 rpm, circulation grinding for 40 min). After the time has elapsed, the samples are cooled down to room temperature, missing formulation components are added to the mill base, and the resulting mixture is homogenized with a dissolver disc.
- 2) Formulation components are mixed in a bottle, which is then closed, clamped in an agitator apparatus (Retsch MM301) and treated at 30 Hz for 40 minutes; in the course of this, the samples heat up. After the time has elapsed, the samples are cooled down to room temperature, missing formulation components are added to the mill base, and the resulting mixture is homogenized with a dissolver disc.

Examples of agrochemical formulations

Examples of agrochemical formulations are shown below.

Table 1: Agrochemical formulation according to the invention (Ethiprole SC 200)

Ingredients	Concentration	Function
Ethiprole	200 g/L	Active Ingredient
Phosphoric esters of polyethoxylated and/or polypropoxylated aryl alcohols	3.67 %w/w	Dispersant
Smectite clay	0.46 %w/w	Rheology modifier
Xanthan Gum	0.23 %w/w	Rheology modifier
Dimethyl siloxanes and silicones	0.28 %w/w	Antifoam
1,2-Propylene Glycol	11.93 %w/w	Antifreeze
Propyl 4-hydroxybenzoate	0.09 %w/w	Biocide
Citric Acid	0.02 %w/w	pH Buffer
Water	To 100%/To 1 liter	Carrier

Preparation of adjuvant formulation

- 5 The adjuvant formulation according to the invention can be prepared in conventional manners, well known to the expert in the art. Some examples of how to prepare these are shown below:

Adjuvant Formulation as self-emulsifiable concentrate

- 10 The components of the adjuvant formulation according to the invention are stirred until a homogeneous solution is obtained. Stirring can be done at any temperature between 20°C-60°C. Dilution with water gives an emulsion.

Adjuvant Formulation as emulsion in water

- 15 Except for water, all other components of the adjuvant formulation according to the invention are stirred until a homogeneous solution is obtained. This solution is added to the corresponding amount of water by means of an emulsifying machine so as to obtain a homogeneous emulsion. The preparation of the emulsion can be done at any temperature between 20°C-60°C.

Examples of adjuvant formulations

Examples of adjuvant formulations according to the invention are shown below.

Table 2: Adjuvant formulations according to the invention

Example	Adjuvant	Adjuvant (%w/w)	Surfactant	Surfactant (%w/w)	Further formulation components	Further formulation components (%w/w)	Liquid Carrier	Liquid Carrier (%w/w)
2-1	Sunflower oil	24.3% (250 g/L)	Synperonic PE/F127 (block copolymer)	4.0%	Biocides KATHON CG/ICP + MPR/PROXEL GXL Antifreeze Glycerin	Biocides 0.08+0.18 Antifreeze 5.0%	Water	To 100%/To 1L
2-2	Marcol 82 (White mineral oil)	25.9% (250 g/L)	Synperonic PE/F127 (block copolymer)	4.0%	Biocides KATHON CG/ICP + MPR/PROXEL GXL Antifreeze Glycerin	Biocides 0.08+0.18 Antifreeze 5.0%	Water	To 100%/To 1L
2-3	Sunflower oil	48.5% (500 g/L)	Synperonic PE/F127 (block copolymer)	4.0%	Biocides KATHON CG/ICP + MPR/PROXEL GXL Antifreeze Glycerin	Biocides 0.08+0.18 Antifreeze 5.0%	Water	To 100%/To 1L
2-4	Rapeseed oil methyl ester	53.2% (500 g/L)	Pluronic PE10500 (block copolymer)	4.0%	Biocides KATHON CG/ICP + MPR/PROXEL GXL Antifreeze Glycerin Antifoam SAG 1572	Biocides 0.08+0.18 Antifreeze 5.0% Antifoam 0.1%	Water	To 100%/To 1L
2-5	Marcol 82 (White mineral oil)	51.5% (500 g/L)	Synperonic PE/F127 (block copolymer)	4.0%	Biocides KATHON CG/ICP + MPR/PROXEL GXL Antifreeze Glycerin	Biocides 0.08+0.18 Antifreeze 5.0%	Water	To 100%/To 1L

Example	Adjuvant	Adjuvant (%w/w)	Surfactant	Surfactant (%w/w)	Further formulation components	Further formulation components (%w/w)	Liquid Carrier	Liquid Carrier (%w/w)
2-6	Rapeseed oil methyl ester	88.0% (800 g/L)	Pluronic PE 6200 (block copolymer) + Nansa EVM 70/2E (alkyl substituted aryl sulfate)	6.0% + 6.0%	n/a	-	n/a	-
2-7	Rapeseed oil methyl ester	90.0% (800 g/L)	Genapol X 080 (linear or branched alcohol ethoxylate)) + Nansa EVM 70/2E (alkyl substituted aryl sulfate)	5.5% + 4.5%	n/a	-	n/a	-
2-8	Rapeseed oil methyl ester	88.0% (800 g/L)	Lutensol TO 12 (linear or branched alcohol ethoxylate)) + Nansa EVM 70/2E (alkyl substituted aryl sulfate)	6.0% + 6.0%	n/a	-	n/a	-
2-9	Innovatti 170 (Soybean Oil methyl ester)	79.1% (720 g/L)	Surfom ADJ 8028 (mixture of linear or branched alcohol ethoxylate and alkyl substituted aryl sulfate)	20.9%	n/a	-	n/a	-

Greenhouse Testing APHIGO (*Aphis gossypii*)*Spray solution preparation*

- 5 The necessary amount of the agrochemical formulation and of the adjuvant formulation was added to the the necessary volume of water (carrier). The resulting mixture was stirred for 5 minutes before being sprayed.

Method Testing APHIGO

Cotton plants (*Gossypium herbaceum*) which were heavily infested by the cotton aphid (*Aphis gossypii*) were treated by being sprayed with the desired concentration of each product. *Aphis gossypii* populations were mainly established on the underside of the leaves.

- 10 Products were applied with a track sprayer application (translaminar application) only the upper side of the leaf was treated.

After the specified period of time, the mortality in % is determined. 100 % means that all the aphids have been killed; 0 % means that none of the aphids have been killed.

Example 1

The agrochemical formulation and the adjuvant formulation were tested as described above, and the results can be found in the table below.

Table 3-Systemic biological activity of the compositions according to the invention

Example	Agrochemical Formulation	Agrochemical Formulation Rate concentration per hectare (L/ha)	Agrochemical Formulation concentration in spray solution (%w/w)	Concentration of active ingredient in spray solution (%w/w)	Adjuvant/Adjuvant Formulation	Adjuvant Formulation Rate concentration per hectare (mL/ha)	Adjuvant Formulation concentration in spray solution (%w/w)	Concentration of adjuvant in spray solution (%w/w)	Agrochemical relevant carrier/rate per hectare (L/ha)	Agrochemical relevant carrier concentration in spray solution (%w/w)	Ratio Adjuvant /Active Ingredient Concentration in spray solution	APHIGO control 1 days after application	APHIGO control 7 days after application
Comparative 3-1	Ethiprole SC 200	0,75 L/ha	0,24938%	0,04988%	-	-	-	-	Water/300 L/ha	99,75062 %	-	10%	22%
Comparative 3-2			0,24933%	0,04987%	Soybean Oil Methyl Ester/2-9	60 mL/ha	0,01995 %	0,01576%		99,73073 %	0,3	8%	26%
Comparative 3-3			0,24913%	0,04983%		300 mL/ha	0,09965 %	0,07872%		99,65122 %	1,6	50%	99%
3-4			0,24876%	0,04975%		750 mL/ha	0,24876 %	0,19652%		99,50249 %	3,9	82%	100%
Comparative 3-5			0,24933%	0,04987%	Rapeseed oil methyl ester/2-4	60 mL/ha	0,01995 %	0,01057%		99,73073 %	0,2	10%	18%
Comparative 3-6			0,24913%	0,04983%		300 mL/ha	0,09965 %	0,13184%		99,65122 %	1,1	44%	96%
3-7			0,24876%	0,04975%		750 mL/ha	0,24876 %	0,05282%		99,50249 %	2,6	87%	100%
Comparative 3-8			0,24933%	0,04987%	Sunflower oil/2-3	60 mL/ha	0,01995 %	0,00957%		99,73073 %	0,2	6%	12%
Comparative 3-9			0,24913%	0,04983%		300 mL/ha	0,09965 %	0,04783%		99,65122 %	1,0	6%	62%

3-10			0,24876%	0,04975%		750 mL/ha	0,24876 %	0,11940%		99,50249 %	2,4	12%	95%
Comparative 3-11			0,24933%	0,04987%	Marcol 82 (White mineral oil)/2-5	60 mL/ha	0,01995 %	0,01037%		99,73073 %	0,2	4%	24%
Comparative 3-12			0,24913%	0,04983%		300 mL/ha	0,09965 %	0,05182%		99,65122 %	1,0	6%	50%
3-13			0,24876%	0,04975%		750 mL/ha	0,24876 %	0,12935%		99,50249 %	2,6	4%	87%

Comments to Table 3

The addition of adjuvant formulations according to the invention allows for the agrochemical formulation according to the invention to exert a systemic activity against aphids. Without adjuvant (comparative example 3-1) the agrochemical formulation shows very limited biological efficacy 1 or 7 days after application. Using soybean oil methyl ester & rapeseed oil methyl ester adjuvant formulations, the systemic activity appears within 1 day after application (examples according to the invention 3-4, 3-7). After 7 days, the systemic activity is visible with all adjuvants (examples according to the invention 3-4, 3-7, 3-10, 3-13).

Additionally, the comparative examples show that when the weight ratio of adjuvant to insecticide in the spray solution is equal to or lower than 1.6, then the systemic activity of the insecticide after 1 day is not satisfactory. With adjuvant formulation 2-9, and a ratio of adjuvant/insecticide of 1.6, the biological control of APHIGO reaches only 50% after 1 day.

With adjuvant formulation 2-3, a weight ratio of adjuvant/insecticide greater than 2.4 ensures that there is sufficient systemic biological efficacy after 7 days (efficacy >90%). With adjuvant formulation 2-4, a weight ratio of adjuvant/insecticide of 2.6 ensures biological efficacy 1 day after application, and full biological control 7 days after treatment. With adjuvant formulation 2-5, a weight ratio of adjuvant/insecticide of 2.6 ensures systemic biological efficacy 7 days after treatment, at a higher level than with a weight ratio of adjuvant/insecticide in the spray solution of 1.0.

Example 2

Table 4-Systemic biological activity of the agrochemical formulation according to the invention and a soybean methyl ester adjuvant formulation according to the invention

Example	Agrochemical Formulation	Agrochemical Formulation Rate concentration per hectare (L/ha)	Agrochemical Formulation concentration in spray solution (%w/w)	Concentration of active ingredient in spray solution (%w/w)	Adjuvant/Adjuvant Formulation	Adjuvant Formulation Rate concentration per hectare (mL/ha)	Adjuvant Formulation concentration in spray solution (%w/w)	Concentration of adjuvant in spray solution (%w/w)	Agrochemical relevant carrier/rate per hectare (L/ha)	Agrochemical relevant carrier concentration in spray solution (%w/w)	Ratio Adjuvant /Active Ingredient Concentration in spray solution	APHI GO control 1 days after application (%)	APHI GO control 7 days after application (%)
4-1	Ethiprol e SC 200	1.25 L/ha	0,41085 %	0,08217 %	Soybean Oil Methyl Ester/2-9	3000	0,98603 %	0,77896 %	Water/300 L/ha	98,6031 2%	9,48	82	93
4-2			0,41391 %	0,08278 %		750	0,24834 %	0,19619 %		99,3377 5%	2,37	74	91
Comparative 4-3			0,41452 %	0,08290 %		300	0,09949 %	0,07859 %		99,4859 9%	0,948	10	78
Comparative 4-4			0,41486 %	0,08297 %		60	0,01991 %	0,01573 %		99,5652 3%	0,1896	0	10
Comparative 4-5			0,41494 %	0,08299 %	-	-	-	-		99,5850 6%	0	0	0
4-6	Ethiprol e SC 200	1.00 L/ha	0,32895 %	0,06579 %	Soybean Oil Methyl Ester/2-9	3000	0,98684 %	0,77961 %	Water/300 L/ha	98,6031 2%	11,85	68	95
4-7			0,33140 %	0,06628 %		750	0,24855 %	0,19635 %		99,3377 5%	2,9625	38	83
Comparative 4-8			0,33190 %	0,06638 %		300	0,09957 %	0,07866 %		99,4859 9%	1,185	0	52

Comparative 4-9			0,33216 %	0,06643 %		60	0,01993 %	0,01574 %		99,5652 3%	0,237	0	0
Comparative 4-10			0,33223 %	0,06645 %	-	-	-	-		99,6677 7%	0	0	0
4-11	Ethiprol e SC 200	0.75 L/ha	0,24691 %	0,04938 %	Soybean Oil Methyl Ester/2-9	3000	0,98765 %	0,78025 %	Water/3 00 L/ha	98,7654 3%	15,8	88	95
4-12			0,24876 %	0,04975 %		750	0,24876 %	0,19652 %		99,5024 9%	3,95	40	91
Comparative 4-13			0,24913 %	0,04983 %		300	0,09965 %	0,07872 %		99,6512 2%	1,58	0	28
Comparative 4-14			0,24933 %	0,04987 %		60	0,01995 %	0,01576 %		99,7307 3%	0,316	0	8
Comparative 4-15			0,24938 %	0,04988 %	-	-	-	-		99,7506 2%	0	0	0
4-16	Ethiprol e SC 200	0.50 L/ha	0,16474 %	0,03295 %	Soybean Oil Methyl Ester/2-9	3000	0,98847 %	0,78089 %	Water/3 00 L/ha	98,8467 9%	23,7	74	94
4-17			0,16598 %	0,03320 %		750	0,24896 %	0,19668 %		99,5850 6%	5,925	44	90
4-18			0,16622 %	0,03324 %		300	0,09973 %	0,07879 %		99,7340 4%	2,37	0	18
Comparative 4-19			0,16636 %	0,03327 %		60	0,01996 %	0,01577 %		99,8136 8%	0,474	0	2
Comparative 4-20			0,16639 %	0,03328 %	-	-	-	-		99,8336 1%	0	0	0
4-21		0.375 L/ha	0,12361 %	0,02472 %		3000	0,98888 %	0,78121 %	Water/3 00 L/ha	98,8875 2%	31,6	84	92

4-22	Ethiprol e SC 200		0,12453 %	0,02491 %	Soybean Oil Methyl Ester/2-9	750	0,24907 %	0,19676 %		99,6264 0%	7,9	20	64
4-23			0,12472 %	0,02494 %		300	0,09978 %	0,07882 %		99,7755 1%	3,16	0	0
Comparative 4-24			0,12482 %	0,02496 %		60	0,01997 %	0,01578 %		99,8552 1%	0,632	0	0
Comparative 4-25			0,12484 %	0,02497 %	-	-	-	-		99,8751 6%	0	0	0

Comments to Table 4

In the absence of agrochemical adjuvant in the spray solution, the agrochemical formulation cannot exert a systemic biological efficacy (cf. comparative examples 4-5, 4-10, 4-15, 4-20, 4-25). The addition of soybean oil methyl ester adjuvant formulations according to the invention allows for the agrochemical
5 formulation according to the invention to exert a systemic activity against aphids. In Table 4 it can be seen that the addition of the adjuvant formulation, if present in a high enough weight ratio with the insecticide concentration in the spray solution, can even lower the concentration of agrochemical formulation needed for efficient control of aphids. For instance, examples 4-1 and 4-21 show the same biological efficacy although in example 4-21, the concentration of the agrochemical formulation is 3 times lower than in
10 example 4-1. This also shows that the higher the concentration of agrochemical formulation in the spray solution, a lower weight ratio of adjuvant/insecticide in the spray solution is needed to obtain a similar systemic biological activity.

Example 3

Table 5-Systemic biological activity of the agrochemical formulation according to the invention and a rapeseed oil methyl ester adjuvant formulation according to the invention.

Examp le	Agroche mical Formulat ion	Agroche mical Formulat ion Rate concentr ation per hectare (L/ha)	Agroche mical Formulat ion concentr ation in spray solution (%w/w)	Concentr ation of active ingredie nt in spray solution (%w/w)	Adjuvant/A djuvant Formulation	Adjuvan t Formula tion Rate concentr ation per hectare (mL/ha)	Adjuvan t Formula tion concentr ation in spray solution (%w/w)	Concentr ation of adjuvant in spray solution (%w/w)	Agroche mical relevant carrier/ra te per hectare (L/ha)	Agroche mical relevant carrier concentr ation in spray solution (%w/w)	Ratio Adjuvan t /Active Ingredie nt Concentr ation in spray solution	APHI GO control 1 days after applic ation (%)	APHI GO control 7 days after applic ation (%)
5-1	Ethiprol e SC 200	1.25 L/ha	0,41085 %	0,08217 %	Rapeseed Oil Methyl Ester/2-7	3000	0,98603 %	0,88743 %	Water/3 00 L/ha	98,6031 2%	10,80	14	90
5-2			0,41391 %	0,08278 %		750	0,24834 %	0,22351 %		99,3377 5%	2,70	0	40
Compar ative 5- 3			0,41494 %	0,08299 %	-	-	-	-		99,5850 6%	-	0	0
5-4													
5-4	Ethiprol e SC 200	1.00 L/ha	0,32895 %	0,06579 %	Rapeseed Oil Methyl Ester/2-7	3000	0,98684 %	0,88816 %	Water/3 00 L/ha	98,6031 2%	13,50	24	88
5-5			0,33140 %	0,06628 %		750	0,24855 %	0,22370 %		99,3377 5%	3,38	0	50
Compar ative 5- 6			0,33223 %	0,06645 %	-	-	-	-		99,6677 7%	-	0	0
5-7	Ethiprol e SC 200	0.75 L/ha	0,24691 %	0,04938 %	Rapeseed Oil Methyl Ester/2-7	3000	0,98765 %	0,88889 %	Water/3 00 L/ha	98,7654 3%	18,00	42	84
5-8			0,24876 %	0,04975 %		750	0,24876 %	0,22388 %		99,5024 9%	4,50	0	22

Comparative 5-9			0,24938 %	0,04988 %	-	-	-	-		99,7506 2%	-	0	0
5-10	Ethiprol e SC 200	0.50 L/ha	0,16474 %	0,03295 %	Rapeseed Oil Methyl Ester/2-7	3000	0,98847 %	0,88962 %	Water/300 L/ha	98,8467 9%	27,00	64	76
5-11			0,16598 %	0,03320 %		750	0,24896 %	0,22407 %		99,5850 6%	6,75	8	64
Comparative 5-12			0,16639 %	0,03328 %	-	-	-	-		99,8336 1%	-	0	0
5-13	Ethiprol e SC 200	0.375 L/ha	0,12361 %	0,02472 %	Rapeseed Oil Methyl Ester/2-7	3000	0,98888 %	0,88999 %	Water (300 L/ha)	98,8875 2%	36,00	58	70
5-14			0,12453 %	0,02491 %		750	0,24907 %	0,22416 %		99,6264 0%	9,00	0	54
Comparative 5-15			0,12484 %	0,02497 %	-	-	-	-		99,8751 6%	-	0	0

Comments to Table 5

In the absence of agrochemical adjuvant in the spray solution, the agrochemical formulation cannot exert a systemic biological efficacy (cf. comparative examples 5-3, 5-6, 5-9, 5-12, 5-15). The addition of rapeseed oil methyl ester adjuvant formulations according to the invention allows for the agrochemical
5 formulation according to the invention to exert a systemic activity against aphids. In Table 5 can be seen that the addition of the adjuvant formulation, if present in sufficient amounts in the spray solution, can even lower the concentration of agrochemical formulation needed for efficient control of aphids. For instance, examples 5-10 and 5-13 show a comparable biological efficacy, although in example 5-13, the concentration of the agrochemical formulation is 75% of the concentration in example 5-10.

Claims:

1. Systemically active compositions comprising:

A) at least one agrochemical formulation of an insecticide active ingredient, the melting point of the insecticide being greater than 75°C, and the water solubility of the insecticide being below 100 mg/L.

B) at least one adjuvant formulation comprising

B1. at least one adjuvant selected from the group of adjuvants b1-b4, wherein

b1 – b4 are selected from the groups comprising:

b1. Vegetable oil esters,

b2. Vegetable oil ethoxylates,

b3. Vegetable oils,

b4. White mineral oils,

B2. at least one surfactant

B3. optionally a liquid carrier

B4. optionally further formulation components, and

C) 82,000% to 99,973% by weight water, based on the total weight of the composition, wherein the weight ratio of the adjuvant to the insecticide in the composition is greater than 1.6.

2. Systemically active composition according to claim 1, wherein the weight ratio of the adjuvant to the insecticide in the composition is greater than 2.3.

3. Systemically active composition according to claim 1 or 2, wherein the insecticide is selected from the group comprising Chlordane, Endosulfan, Ethiprole and Fipronil.

4. Systemically active composition according to one or more of claims 1-3, wherein the insecticide is selected from the group comprising Ethiprole and Fipronil.

5. Systemically active composition according to one or more of claims 1-4, wherein the insecticide is selected from the group comprising Ethiprole.

6. Systemically active composition according to one or more of claims 1-5 further comprising an insecticide selected from the group comprising Acetamiprid, Clothianidin, Dinotefuran, Imidacloprid, Nitenpyram, Thiacloprid, Thiamethoxam, Nicotine, Sulfoxaflor, Flupyradifurone, Triflumezopyrim and Flupyrimin.

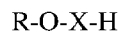
7. Systemically active composition according to one or more of claims 1-6 further comprising Imidacloprid.
8. Systemically active composition according to one or more of claims 1-7 wherein the surfactant B2 is selected from the group comprising

5 B2.1. Anionic surfactants in the form of

B2.1.1. Calcium dodecyl benzene sulfonate and corresponding salts thereof

B2.2. Non-ionic surfactant in the form of at least one of the classes which comprises

B2.2.1. linear or branched alcohol ethoxylate, as represented in Formula I,



10 (I)

wherein R is a linear or branched C12-C16 alkyl radical, and X is a polyethylene glycol block, consisting of 6 to 13 ethylene oxide (formula III-b) units

B2.2.2. block copolymer, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being represented as in Formula II.

15 H-A-B-A-H

(II)

wherein B is a polypropylene glycol fragment consisting of 50 to 70 propylene oxide (PO) units (formula III-a and A is a polyethylene glycol fragment consisting of 35 to 110 ethylene oxide (EO) units (formula III-b).

- 20 9. Systemically active composition according to one or more of claims 1-8 comprising at least one adjuvant selected from the group of b1 vegetable oil esters.
 10. Systemically active composition according to one or more of claims 1-9 wherein b1-b4 is selected from the group comprising linear and/or branched alkyl esters of C10-C24 saturated and unsaturated fatty acids of vegetable or mineral origin: e.g. methyl, ethyl, propyl, butyl, pentyl, hexyl, isopropyl, isobutyl, isopentyl, 2-ethyl hexyl esters of capric acid, undecylic acid, lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, nonadecylic acid, arachidic acid, heneicosylic acid, behenic acid, tricosylic acid, lignoceric acid, α -Linolenic acid, linoleic acid, linolelaidic acid, palmitoleic acid, oleic acid, erucic acid.
- 25

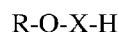
11. Systemically active composition according to one or more of claims 1-10 wherein b1-b4 is selected from the group comprising C1-C2 ester of sunflower oil, rapeseed oil, corn oil, soybean oil, rice bran oil, olive oil.

12. Systemically active composition according to one or more of claims 1-11, wherein

5 the adjuvant B1 is selected from rapeseed oil methyl ester and soybean oil methyl ester, and the surfactant B2 is selected from the group consisting of

B2.1.1. calcium dodecyl benzene sulfonate and corresponding salts thereof

B2.2.1. linear or branched alcohol ethoxylates, as represented in Formula I,



10 (I)

wherein R is a linear or branched C12-C16 alkyl radical, and X is a polyethylene glycol block, consisting of 6 to 13 ethylene oxide units, and

B2.2.2. block copolymers, made up of a polyethylene glycol block (A) joined to a polypropylene glycol (B) block joined to a polyethylene glycol block (A), this being represented as in Formula II.

15 H-A-B-A-H

(II)

wherein B is a polypropylene glycol fragment consisting of 50 to 70 propylene oxide (PO) units and A is a polyethylene glycol fragment consisting of 35 to 110 ethylene oxide (EO) units.

13. Systemically active composition according to claim 12 comprising ethiprole.

20 14. Systemically active composition according to one or more of claims 1-13 wherein b1-b4 is soybean oil methyl ester.

15. Use of a systemically active composition according to any of claims 1-14 against animal pests from the families of Aphididae, Curculionidae, Cercopidae, Pentatomidae, Cicadellidae, Thripidae, Aleyrodidae, Tetranychidae preferably in cotton, soybean, corn, coffee, sugar cane, sorghum, 25 vegetables.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/055209

A. CLASSIFICATION OF SUBJECT MATTER INV. A01N25/04 A01P7/04 ADD.		
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) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2023/114120 A1 (FMC CORP [US]) 22 June 2023 (2023-06-22) examples -----	1-15
X	WO 2021/067678 A1 (FMC CORP [US]; FMC AGRO SINGAPORE PTE LTD [SG]) 8 April 2021 (2021-04-08) examples 9-10 -----	1, 2, 8-12, 14, 15
Y		1-15
X	US 9 332 756 B2 (GUTSCHE OLIVER WALTER [US]; ANNAN ISAAC BILLY [US] ET AL.) 10 May 2016 (2016-05-10) table 2 -----	1, 2, 8-12, 14
Y		1-15
X	WO 2008/031512 A1 (BAYER CROPSCIENCE AG [DE]; VERMEER RONALD [DE] ET AL.) 20 March 2008 (2008-03-20) examples -----	1, 6-8
Y		1-15
☐ 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 2 May 2024		Date of mailing of the international search report 13/05/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Bertrand, Franck

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