

A FORMULATION USEFUL FOR SPRAYING

Field of the invention

5 The present invention relates to stable formulations suitable for spraying useful substances, for example, as insecticide, herbicide, fungicide, insect repellent, deodoriser and/or drug administration.

Background of the invention

10 Formulations suitable for spraying are well known. For example, EP0331474 A1 describes spray formulations comprising an oil phase comprising active ingredient, an emulsifier and an evaporation retardant.

However, oil in water emulsions (EW) have the problem of instability which may compromise the efficacy of such formulations when used as spray formulations. In particular, instability leads to increasing EW particle sizes over time and poor shelf life.

15 Accordingly, there is a need to make more stable sprayable EW formulations.

Summary of the invention

The present invention addresses the above problems, and in particular provides new formulations with improved stability.

20 According to a first aspect of the present invention, there is provided a formulation suitable for spraying comprising an oil phase comprising at least one active ingredient and a stabiliser, wherein the stabiliser comprises at least one epoxidised vegetable oil, and optionally at least one emulsifier and/or a vapour retardant additive.

25 According to another aspect of the present invention, there is provided a method of preparing a formulation according to any aspect of the present invention, comprising preparing an oil phase comprising at least one active ingredient and a stabiliser, wherein the stabiliser comprises at least one epoxidised vegetable oil, and optionally at least one emulsifier and/or a vapour retardant additive.

According to another aspect of the present invention, there is provided a spray container comprising the formulation according to any aspect of the present invention.

According to another aspect of the present invention, there is provided a use of the formulation according to any aspect of the present invention, optionally diluted with water, or a use of the spray container according to any aspect of the present invention, to control insects, acarine pests or unwanted plants.

Brief description of the figures

Figure 1 shows results of a stability test conducted for two formulations, one comprising a stabilizer and the other not comprising a stabilizer. Particle sizes for the two formulations were measured over 24 months to compare their relative stability. In particular, Fig. 1(a) shows the particle size volume median diameter of formulation FI-09138 (or "Composition 1") not comprising a stabilizer and Fig. 1(b) shows the particles size volume median diameter of formulation FI-09139 (or "Comparative Composition 1") comprising epoxidised soybean oil (commercially available as Amepon SB/65) as a stabilizer at 0.55% w/w. The volume median diameter $d(v,0.5)$ is the diameter where 50% of the particle size distribution is above and 50% is below as volume basis.

Preparation steps for the two formulations compared may be found in the Examples, namely Manufacturing Example 1 (with stabilizer) and Comparative Manufacturing Example 1 (without stabilizer).

Figure 2 shows results of the evaporation retardation profiles of two formulations in comparison with a commercial standard, Aqua Resigen EW (Bayer Crop Science). The two formulations are FI-10077 (or "Composition 1", including vapour retardant) and FI-10078 (or "Comparative Composition 2", not including Vapour Retardant). To evaluate evaporation retardation profile same as the description in EP0331474 A1, a droplet of diluted emulsion is suspended on a fine wire over a petri dish and its cross-sectional area is measured under a microscope over 10 minutes. This may be repeated at different dilutions for a given formulation. In figure 2, this test was conducted for a 10 times water dilution of the formulations. Preparation steps for the two formulations

compared may be found in the Examples, namely Manufacturing Example 1 (with vapour retardant) and Comparative Manufacturing Example 2 (without vapour retardant).

Detailed description of the invention

- 5 The embodiments of the present invention are primarily concerned with stable formulations suitable for spraying useful substances, for example, insecticide, herbicide, fungicide, acaricide, insect repellent, insect growth regulator, plant growth regulator, dye, perfume, bactericide, lubricant, medicament, paint, polish lacquer, textile treatment, deodoriser and/or drug.
- 10 Taking the example of an insecticide formulation, some embodiments of the present invention may be concerned with an oil-in-water formulation suitable for spraying or for dilution with water to form a spray formulation for indoor and outdoor use in the field of public health, or pest and vector control. For instance, these sprayable formulations may be in the form of an ultra low volume spray or thermal fog space spray.
- 15 The terms "a" and "an" are used herein to refer to one or to more than one (i.e. at least one) of the grammatical object of the article. By way of example, "an element" means one element or more than one element.

20 An emulsion is a mixture of two or more liquids that are normally immiscible. In an emulsion, one or more liquids (the dispersed phase) is dispersed in the other (the continuous phase). This may happen for example after vigorous mixing, homogenization or even exposing the immiscible liquids to ultrasound energy. "Oil in water emulsions" thus refer to emulsions comprising an oil phase dispersed within an aqueous phase. Due to the immiscible nature of the liquids, many emulsions are unstable and tend to separate into different phases over time, for example an oil in water emulsion may
25 separate into an oil phase and an aqueous phase.

Oil in water emulsions may be made more stable by adding emulsifiers, such as commercially available emulsifiers and surfactants like those available under the trade name BRIJ (<http://www.sigmaaldrich.com/materials-science/material-science-products.html?TablePage=9541703>) and Genapol
30 (<http://www.essentialingredients.com/pdf/GenapolO200TechnicalDataSheet.pdf>). However, typical formulations comprising such emulsifiers and surfactants still exhibit

instability in particle sizes. One example can be seen from Fig. 1(a), which shows the volume median diameter for a formulation without a stabilizer increases over time, indicating instability in particle sizes.

The term “pest control” refers to the regulation or management of a pest, usually because it is perceived to be detrimental to the health of a subject, the ecology or the economy. In particular, controlling a species of pests refers to maintaining the population of the species of pests at a level that is not detrimental to the health of a subject, the ecology or the economy.

Examples of noxious pests (noxious insects/acarina) against which the present compound exhibits a control effect include the following:

Hemiptera

Delphacidae (planthoppers) such as *Laodelphax striatellus* (small brown planthopper), *Nilaparvata lugens* (brown planthopper), *Sogatella furcifera* (white backed rice planthopper); leafhoppers such as *Nephotettix cincticeps*, *Nephotettix virescens*; Aphididae (aphids); plant bugs; Aleyrodidae (whiteflies); scales; Tingidae (lace bugs); Psyllidae; and so on;

Lepidoptera

Pyralidae such as *Chilo suppressalis* (rice stem borer), *Cnaphalocrocis medinalis* (rice leafroller), *Plodia interpunctella* (Indian meal moth); Noctuidae such as *Spodoptera litura* (tobacco cutworm), *Pseudaletia separata* (rice armyworm), *Mamestra brassicae* (cabbage armyworm); Pieridae such as *Pieris rapae crucivora* (common cabbageworm), Tortricidae such as *Adoxophyes* spp.; Carposinidae; Lyonetiidae; Lymantriidae; Plusiinae; *Agrotis* spp. such as *Agrotis segetum* (turnip cutworm), *Agrotis epsilon* (black cutworm); *Helicoverpa* spp.; *Heliotis* spp.; *Plutella xylostella* (diamondback moth); *Parnara guttata* (rice skipper); *Tinea pellionella* (casemaking clothes moth); *Tineola bisselliella* (webbing clothes moth); and so on;

Diptera

Culex spp. such as *Culex pipiens pallens* (common mosquito), *Culex tritaeniorhynchus*; *Aedes* spp. such as *Aedes aegypti*, *Aedes albopictus*; *Anopheles* spp. such as *Anopheles sinensis*; Chironomidae (midges); Muscidae such as *Musca domestica* (housefly), *Muscina stabulans* (false stablefly); Calliphoridae; Sarcophagidae;

Anthomyiidae such as *Delia platura* (seedcorn maggot), *Fannia canicularis* (little housefly), *Delia antiqua* (onion maggot); Tephritidae (fruit flies); Drosophilidae; Psychodidae (moth flies); Tabanidae; Simuliidae (black flies); Stomoxyidae; and so on;

Coleoptera (beetles)

- 5 corn rootworms such as *Diabrotica virgifera* (western corn rootworm), *Diabrotica undecimpunctata howardi* (southern corn rootworm); Scarabaeidae such as *Anomala cuprea* (cupreous chafer), *Anomala rufocuprea* (soybean beetle); weevils such as *Sitophilus zeamais* (maize weevil), *Lissorhoptrus oryzophilus* (ricewater weevil), ball weevil, *Callosobruchus chinensis* (adzuki bean weevil); Tenebrionidae (darkling beetles)
- 10 such as *Tenebrio molitor* (yellow mealworm), *Tribolium castaneum* (red flour beetle); Chrysomelidae (leaf beetles) such as *Oulema oryzae* (rice leaf beetle), *Phyllotreta striolata* (striped flea beetle), *Aulacophora femoralis* (cucurbit leaf beetle); Anobiidae; *Epilachna* spp. such as *Epilachna vigintioctopunctata* (twenty-eight-spotted ladybird); Lyctidae (powderpost beetles); Bostrychidae (false powderpost beetles); Cerambycidae;
- 15 *Paederus fuscipes* (robe beetle); and so on;

Dictyoptera

Blattella germanica (German cockroach); *Periplaneta fuliginosa* (smokybrown cockroach); *Periplaneta americana* (American cockroach); *Periplaneta brunnea* (brown cockroach); *Blatta orientalis* (oriental cockroach); and so on;

- 20 Thysanoptera

Thrips palmi; western flower thrips; *Thrips hawaiiensis*; and so on;

Hymenoptera

Formicidae (ants); Vespidae (hornets); Bethyidae; Tenthredinidae (sawflies) such as *Athalia rosae ruficornis* (cabbage sawfly); and so on;

- 25 Orthoptera

Gryllotalpidae (mole crickets); Acrididae (grasshoppers); and so on;

Siphonaptera

Pulex irritans; *Ctenocephalides felis* (cat flea); and so on;

Anoplura

Pediculus humanus humanus (body louse); *Pthirus pubis* (crab louse); and so on;

Isoptera

- 5 *Reticulitermes speratus*, *Coptotermes formosanus* (Formosan subterranean termite); and so on;

House-dust Mites

- 10 Dermanyssidae such as *Dermatophagoides farinae* (American house dust mite), *Dermatophagoides pteronyssinus*; Acaridae such as *Tyrophagus putrescentiae* (mold mite), *Aleuroglyphus ovatus*; and so on;

The Other Mites

- 15 Glycyphagidae such as *Glycyphagus privatus*, *Glycyphagus domesticus*, *Glycyphagus destructor*; Cheyletidae such as *Chelacaropsis malaccensis*, *Cheyletus fortis*; Tarsonemidae; *Chortoglyphus* spp.; *Haplochthonius simplex* and the like;
- 15 Tetranychidae such as *Tetranychus urticae* (carmine spider mite); *Tetranychus kanzawai* (Kanzawa spider mite); *Panonychus citri* (citrus red mite); *Panonychus ulmi* (European red mite); and so on;

Ticks

Ixodidae such as *Haemaphysalis longiconis*;

- 20 The term "subject" includes both human and animal subjects and parts thereof. Animal subjects include but are not limited to mammals, household pets and livestock animals. The animal subjects may include but are not limited to dogs, cats, birds, horses, cattle, pigs, sheep, goats, chicken, duck and turkey.
- 25 According to a first aspect of the present invention, there is provided a formulation suitable for spraying comprising an oil phase comprising at least one active ingredient and a stabiliser, wherein the stabiliser comprises at least one epoxidised vegetable oil, and optionally at least one emulsifier and/or a vapour retardant additive.

The term "comprising" is herein defined as "including principally, but not necessarily solely". Further, the term "comprising" will be automatically read by the person skilled in the art as including "consisting of". The variations of the word "comprising", such as "comprise" and "comprises", have correspondingly varied meanings.

- 5 By adding a stabilizer, such as an epoxidised vegetable oil, formulations according to any aspect of the present invention have an excellent improvement in particle size distribution stability over time and over a range of temperatures. One example of such an epoxidised vegetable oil may be epoxidised soybean oil, such as is commercially available from suppliers like Ametech SRL, under the product name of Amepon SB/65
10 (http://www.ametech.it/pr_agro_ad_stabilizing_agents_print.php).

As may be seen from Fig. 1(a), a formulation without a stabilizer shows a rapid increase of the volume median diameter over time and over a range of different temperatures, indicating instability in particle sizes. In comparison, Fig. 1(b) shows that formulations with a stabilizer maintain a relatively stable particle size when stored at the same range
15 of temperatures. Comparing volume median diameters of the two formulations, particle sizes were larger for the prior art composition over most of the two-year period, at all storage conditions / temperatures tested. Preparation steps for the two formulations compared may be found in the Examples, namely Manufacturing Example 1 (with stabilizer) and Comparative Manufacturing Example 1 (without stabilizer).

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However, it is understood that embodiments of the present invention are not limited to embodiments wherein the stabilizer is epoxidised soybean oil. For example, embodiments of the present invention may comprise at least one epoxidised vegetable oil derived from at least one vegetable oil selected from the group consisting of soybean
25 oil, Jatropha oil, lindseed oil, neem oil, palm oil, coconut oil, cottonseed oil, peanut oil, olive oil, rapeseed oil, safflower oil, sesame oil, sunflower oil, almond oil, beechnut oil, cashew oil, hazelnut oil, macadamia oil, mongongo oil, pecan oil, pine nut oil, pistachio oil, and walnut oil. In some embodiments, the stabilizer is epoxidised soybean oil.

Embodiments of the present invention may further comprise an aqueous phase
30 comprising at least one dispersing agent and optionally at least one antifoam agent and/or thickening agent.

In some embodiments of the present invention, the formulation may further comprise an aqueous phase comprising at least one dispersing agent. In some embodiments, the formulation may further comprise at least one selected from the group consisting of antifoam agents and thickening agents.

- 5 Dispersing agents are substances added to a suspension, a colloid or an emulsion, to improve the separation of particles and to prevent settling or clumping of particles. For example, some embodiments of the present invention may comprise one or more dispersing agents such as polyvinyl alcohol (available commercially for example Gohsenol GL-05 from Gohsenol.com), Arabic Gum, Lignosulphonate sodium salt and/or
10 polycarboxylic acid sodium salt.

- An antifoam agent is a substance that reduces and hinders the formation of foam. For example, some embodiments of the present invention may comprise one or more antifoam agents such as active silicone polymer or the like. Commercially available examples may include Antifoam C emulsion (Dow Corning Asia, Corp.) and/or
15 Silcolapse 5000 (Rhodia).

- Thickening agents are substances which increase the viscosity of a solution or liquid/solid mixture. Suitable thickening agents may include Xanthan gums and Mineral silicates. For example, some embodiments of the present invention may comprise one or more thickening agents such as Veegum G (magnesium aluminum silicate from R.T. Vanderbilt) , Kelzan S (xanthan gum available from CP Kelco), Carboxy methyl cellulose,
20 Carageenan and/or Guar gum.

- To extend the shelf-life of the proposed formulations, some embodiments of the present invention may also comprise preservatives such as 1,2 Benzisothiazolin-3-one (available commercially from Lonza as Proxel GXL) and/or mixture of 5-chloro-2-methyl-4-
25 isothiazolin-3-on, 2-methyl-4-isothiazolin-3-one and bronopol(available commercially from KI Kasei as Biohope L).

- The term “optionally” with respect to any element of a claim or a phrase is intended to mean that the subject element is required, or alternatively, is not required. Both alternatives are intended to be within the scope of the claim or phrase. Use of broader
30 terms such as comprises, includes, having, etc. should be understood to provide support for narrower terms such as consisting of, consisting essentially of, comprised substantially of, etc.

It is understood that the embodiments of the present invention are not limited to pesticide formulations. Therefore, embodiments of the present invention may comprise at least one active ingredient selected from the group consisting of an insecticide, herbicide, fungicide, acaricide, insect repellent, insect growth regulator, plant growth regulator, dye, perfume, bactericide, lubricant, medicament, paint, polish lacquer, textile treatment, deodoriser and drug.

For the purposes of this specification, the term "active ingredient" is used to mean any biologically active substance such as a compound which is able to assert the desired biological effect, for example an insecticidal, herbicidal, fungicidal, acaricidal, insect-repellent, deodorising, and/or therapeutic effect. For the purposes of this specification, the term "active ingredient" is also understood to include synergist or adjuvants.

A synergist or adjuvant is any agent suitable for modifying the effect of other agents, such as an insecticide, herbicide, fungicide, acaricide, insect repellent, insect growth regulator, plant growth regulator, dye, perfume, bactericide, lubricant, medicament, paint, polish lacquer, textile treatment, deodoriser and/or drug. For example, synergists or adjuvants may be used in combination with herbicides, insecticides, fungicides and other pesticidal agents that control or eliminate unwanted pests, in order to enhance their effectiveness. Synergists or adjuvants may not be themselves effective in controlling or killing pests, or in providing therapy. Instead, synergists or adjuvants may exert an effect on the pest or disease indication, such that the ability of the pesticide or drug to penetrate, target or protect the target organism is enhanced. For example, it is believed that the pesticide synergist Piperonyl butoxide may inhibit the breakdown of pesticidal compounds in insects. Therefore, inhibiting this breakdown allows higher concentrations of the pesticide (such as a pyrethroid compound) to remain within the target pest for a longer period (<http://npic.orst.edu/factsheets/pbogen.pdf>). Accordingly, the formulations of the present invention may also comprise one or more adjuvants.

The formulations of the present invention may also comprise one or more additives such as surfactants, emulsifiers, vapour retardants, oils and salts. These additives may be able to improve such formulation properties as spreading, penetration, droplet size or other characteristics. For example, some embodiments of the present invention may be diluted in water to be used in an ultra low volume (ULV) or thermal fog space spray. Such applications may require the sprayed droplets to travel over a long distance (~100 m) with minimum water evaporation so as to hit target areas or pests at a desirable droplet size. To achieve minimum water evaporation, the formulations of the present

invention may comprise one or more vapour retardants. Vapour retardants are substances able to retard the evaporation of the water from the drops of the spray in particular in a formulation prepared for spraying over a target area. The target area may have a population of pests perceived to be detrimental to the health of a subject, the ecology or the economy. Vapour retardants are well known in the preparation of formulations for spraying. For example, EP0331474 A1 describes a formulation suitable for spraying comprising an oil phase comprising active ingredient, an emulsifier and an evaporation retardant. Embodiments of the present invention may comprise one or more additives, for example at least one vapour retardant. In particular, formulations of the present invention may comprise more than one vapour retardant such as cetyl alcohol and/or at least one fatty acid. More in particular, the at least one fatty acid may comprise stearic acid and/or palmitic acid.

As may be seen from Fig. 2, a formulation without a vapour retardant shows a rapid decrease in droplet cross-sectional area over a period of 10 minutes. In comparison, a formulation with vapour retardants maintains a relatively stable droplet cross-sectional area over the same period. The evaporation retardation profile of the formulation with vapour retardants is similar to that of a commercial standard, Aqua Resigen EW (Bayer Crop Science). Preparation steps for the two formulations compared may be found in the Examples, namely Manufacturing Example 1 (with vapour retardant) and Comparative Manufacturing Example 2 (without vapour retardant).

In some embodiments of the present invention, the formulation may comprise an active ingredient wherein the active ingredient comprises at least one pyrethroid compound.

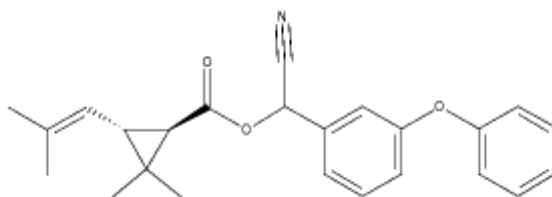
In general, pyrethroid compounds are roughly divided into the so-called knock-down agent superior in a knock-down effect, and the so-called killing agent superior in a lethal effect. Examples of knock-down and killing agents include metofluthrin and cyphenothrin, respectively. Practically, it is desirable to have both knock-down and killing effects in an insecticide, but at present there are not known single pyrethroid compounds having both effects which are cost-effective.

In particular embodiments of the present invention related to pesticide formulations, formulations according to any aspect of the present invention may comprise as the active ingredient at least one pyrethroid compound and optionally at least one pesticide synergist. The pyrethroid compound may be selected from the group consisting of

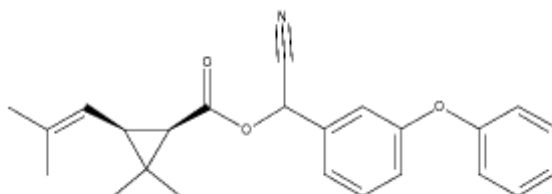
allethrin, phthalthrin, prallethrin, furamethrin, empenthrin, phenothrin, permethrin, cyphenothrin, cypermethrin, decamethrin, tralomethrin, deltamethrin, bifenthrin, cyfluthrin, etofenprox, transfluthrin, cycloprothrin, acrinathrin, fenvalerate, esfenvalerate, flucythrinate, tefluthrin, esbiothrin, fenpropathrin, tetramethrin, fluvalinate, cyhalothrin, resmethrin, meperfluthrin, teflumethrin, dimefluthrin, Pyrethrin I, Pyrethrin II, Cinerin I, Cinerin II, jasmolin I, jasmolin II and metofluthrin. In particular, the at least one active ingredient may comprise cyphenothrin and/or metofluthrin and optionally piperonyl butoxide.

Cyphenothrin is the common name of a pyrethroid insecticide with IUPAC name: [cyano-(3-phenoxyphenyl)methyl]-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropane-1-carboxylate. It is also known by the trade name GOKILAHT and has the following structural formula and identifiers:

Structural Formula:



(1R)-*trans*-isomer



15 (1R)-*cis*-isomer

NOMENCLATURE

Common name cyphenothrin (see Composition) (BSI, E-ISO); cyphénothrine ((f) F-ISO)

IUPAC name (RS)- α -cyano-3-phenoxybenzyl (1RS,3RS;1RS,3SR)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate (see Composition)

Roth: (RS)- α -cyano-3-phenoxybenzyl (1R)-*cis-trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate

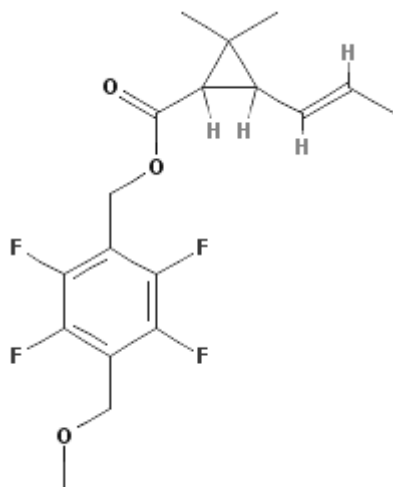
Chemical Abstracts name cyano(3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate Other names d-cyphenothrin CAS RN [39515–40–7] unstated stereochemistry EC no 254–484–5 Development codes S-2703 Forte (Sumitomo Chemical)

Smiles code: N#CC(OC(=O)C1C(/C=C(/C)C)C1(C)C)c3cccc(Oc2ccccc2)c3

For the purposes of this specification, the term “Cyphenothrin” is to be understood to mean either an optically pure enantiomer of Cyphenothrin or a mixture of enantiomers of Cyphenothrin. For example, embodiments of the present invention may comprise S- and

R- enantiomers of Cyphenothrin in varying degrees of enantiomeric excess. In particular, some embodiments of the present invention may comprise racemic Cyphenothrin as the active ingredient and other embodiments may comprise the S-enantiomer of Cyphenothrin, known by trade name GOKILAHT-S as the active ingredient.

- 5 Metofluthrin is the common name of a pyrethroid insecticide with IUPAC name: 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl (E)-2,2-dimethyl-3-prop-1-enylcyclopropanecarboxylate. It is also known by the trade name SUMIONE and has the following structural formula and identifiers:



Structural Formula:

NOMENCLATURE

Common name metofluthrin (BSI, E-ISO); métoluthrine ((f) F-ISO)

IUPAC name 2,3,5,6-tetrafluoro-4-(methoxymethyl)benzyl (E)-2,2-dimethyl-3-prop-1-enylcyclopropanecarboxylate, but see Composition

Chemical Abstracts name [2,3,5,6-tetrafluoro-4-(methoxymethyl)phenyl]methyl 2,2-dimethyl-3-(1-propenyl)cyclopropanecarboxylate CAS RN [240494-70-6] Development codes S-1264 (Sumitomo Chemical) Smiles code without stereochemistry: COCc1c(F)c(F)c(COC(=O)C2C(C=CC)C2(C)C)c(F)c1F

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Formulations of the present invention comprising insecticidal active ingredients have shown better kill and knockdown efficacy as compared to the prior art, based on laboratory tests and field trials data conducted in Malaysia & Turkey.

- 15 According to another aspect of the present invention, there is provided a spray container comprising the formulation according to any aspect of the present invention.

Embodiments of the present invention relating to insecticidal formulations are mainly used for preparing liquid agents such as oil sprays, emulsifiable concentrates and aerosols. They may also be used for preparing mosquito coils, mat for electric fumigators, other fumigants, non-heating volatile formulations applied on resin or paper, fogging formulations, poisonous bait, granules, dusts and UVL formulations (formulations for ultra low volume application).

According to another aspect of the present invention, there is provided a method of preparing a formulation suitable for spraying, comprising preparing an oil phase comprising at least one active ingredient and a stabiliser, wherein the stabiliser comprises at least one epoxidised vegetable oil, and optionally at least one emulsifier and/or a vapour retardant additive.

In some embodiments, the method further comprises adding an aqueous phase comprising at least one dispersing agent and optionally at least one antifoam agent and/or thickening agent.

In some embodiments, the method may comprise steps:

- (i) Mixing and heating the oil phase in order to dissolve components of the oil phase;
- (ii) Mixing and heating the aqueous phase in order to dissolve components of the aqueous phase;
- (iii) Mixing and heating the thickening solution in order to dissolve components of the thickening solution;
- (iv) cooling each of the oil phase, aqueous phase and thickening solution;
- (v) adding the oil phase to the aqueous phase gradually under stirring to form a mixture;
- (vi) homogenizing the mixture of step (v) to obtain a homogenized mixture;
- (vii) mixing the thickening solution with the homogenized mixture to form the insecticide formulation.

For the purposes of this specification, the terms “ambient temperature”, “room temperature”, “ambient conditions” and “tropical conditions” are used interchangeably to refer to ambient room temperatures experienced in tropical countries, i.e. approximately $30^{\circ}\text{C} \pm 4^{\circ}\text{C}$, preferably approximately $30^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

In some embodiments, the method may comprise preparing an oil phase comprising at least one stabilizer, wherein the stabilizer may comprise at least one epoxidised vegetable oil, wherein the at least one epoxidised vegetable oil is derived from at least one vegetable oil selected from the group consisting of soybean oil, Jatropha oil, lindseed oil, neem oil, palm oil, coconut oil, cottonseed oil, peanut oil, olive oil, rapeseed oil, safflower oil, sesame oil, sunflower oil, almond oil, beechnut oil, cashew oil, hazelnut oil, macadamia oil, mongongo oil, pecan oil, pine nut oil, pistachio oil, and walnut oil.

In some embodiments, the stabiliser is epoxidised soybean oil.

In some embodiments, the method may comprise preparing an oil phase comprising at least one active ingredient, wherein the active ingredient is at least one selected from the group consisting of an insecticide, herbicide, fungicide, acaricide, insect repellent, deodoriser and drug.

In some embodiments, the active ingredient comprises at least one pyrethroid.

In some embodiments, the pyrethroid compound is selected from the group consisting of allethrin, phtalthrin, prallethrin, furamethrin, empenethrin, phenothrin, permethrin, cyphenothrin, cypermethrin, decamethrin, tralomethrin, deltamethrin, bifenthrin, cyfluthrin, etofenprox, transfluthrin, cycloprothrin, acrinathrin, fenvalerate, esfenvalerate, flucythrinate, tefluthrin, esbiothrin, fenpropathrin, tetramethrin, fluvalinate, cyhalothrin, resmethrin, meperfluthrin, teflumethrin, dimefluthrin, Pyrethrin I, Pyrethrin II, Cinerin I, Cinerin II, jasmolin I, jasmolin II and metofluthrin.

In some embodiments, the formulation may comprise cyphenothrin and/or metofluthrin and optionally piperonyl butoxide.

According to another aspect of the present invention, there is provided a use of the formulation according to any aspect of the present invention, optionally diluted with water, or a use of the spray container according to any aspect of the present invention to control insects, acarine pests or unwanted plants

Having now generally described the invention, the same will be more readily understood through reference to the following examples which are provided by way of illustration, and are not intended to be limiting of the present invention.

EXAMPLES

Hereinafter, the present invention will be described in more detail by way of preparation examples and test examples to which the present invention is not limited. In the following examples, the terms “part (s)” means by weight.

5 Manufacturing example 1

Composition 1 is obtained by the following steps:

An oil phase was prepared by dissolving 0.1 parts by weight of metofluthrin, 6 parts by weight of Cyphenothrin and 10 parts by weight of piperonyl butoxide into 9.45 parts by weight of aromatic hydrocarbon solvent. And further, 0.55 parts by weight of stabilizer
 10 (epoxidised soybean oil), 2.25 parts by weight of vapour retardant additive A (cetyl alcohol), 0.75 parts by weight of vapour retardant additive B (mixture of stearic acid and palmitic acid), 0.6 parts by weight of emulsifier A (Genopol O 200, product name of Clariant Int. Ltd.), 0.46 parts by weight of emulsifier B (Brij S20-PA-SG, product name of CRODA SINGAPORE. PTE LTD) and 0.94 parts by weight of emulsifier C (Brij O10-SS-
 15 RB, product name of CRODA EUROPE LTD, Rawcliffe Bridge, UK) were added and mixed by stirring to obtain an oil phase.

Separately from the above-described preparation of oil phase, an aqueous phase was prepared by dissolving 1.5 parts by weight of polyvinyl alcohol into 45 parts by weight of deionised water. And further, 0.1 parts by weight of anti-foam agent (Antifoam
 20 C, product name of Dow Corning Asia, Corp.) was added and mixed by stirring to obtain a polyvinyl alcohol aqueous phase.

Separately from the above-described preparations of oil phase and aqueous phase, 0.2 parts by weight of preservative additives (1,2-benzisothiazoline-3-one), 0.15 parts by weight of thickening agent (aluminium magnesium silicate), 0.075 parts by weight of thickening agent (xanthane gum) and 14 parts by weight of deionised water
 25 were mixed by stirring to obtain a thickening solution.

An oil-in-water emulsion was obtained by adding 46.6 parts by weight of an aqueous phase to 32 parts by weight of above-described oil phase, agitating it for 90 minutes at 3000rpm to emulsify and disperse it. 14.425 parts by weight of above-
 30 described thickening solution was added to the obtained oil-in-water emulsion and, further, 6.975 parts by weight of deionised water was added to make a total amount of the composition 1.

Manufacturing example 2

Composition 2 is obtained by preparing exactly similar to Manufacturing example 1 except that 9.45 parts by weight of aromatic hydrocarbon solvent of Manufacturing example 1 is changed to 9.45 parts by weight of 1-phenyl-1-xylylethane.

5 Manufacturing example 3

Composition 3 is obtained by preparing exactly similar to Manufacturing example 1 except that 9.45 parts by weight of aromatic hydrocarbon solvent of Manufacturing example 1 is changed to 9.45 parts by weight of 1-phenyl-1-ethylphenylethane.

Manufacturing example 4

10 Composition 4 is obtained by the following steps:

A uniform oil phase solution is prepared by placing 0.15 parts by weight of metofluthrin, 7.5 parts by weight of Cyphenothrin and 15 parts by weight of piperonyl butoxide and 15 parts by weight of aromatic hydrocarbon solvent. And further, 0.75 parts by weight of stabilizer (epoxidised soybean oil), 4.0 parts by weight of vapour retardant additive (cetyl alcohol), 0.8 parts by weight of emulsifier A (Genopol O 200, product name of Clariant Int. Ltd.), 1.8 parts by weight of emulsifier C (Brij O10-SS-RB, product name of CRODA EUROPE LTD, Rawcliffe Bridge, UK) are added and agitated by stirring to obtain an oil phase.

20 An aqueous phase is prepared by putting 40 parts by weight of deionised water, 0.1 parts by weight of anti-foam agent (Antifoam C, product name of Dow Corning Asia, Corp.), and 1.5 parts by weight of polyvinyl alcohol into another container, and agitating it.

25 An oil-in-water emulsion is obtained by adding 45 parts by weight of the above-described oil phase to 41.6 parts by weight of the above-described aqueous phase, and further, agitating it for 90 minutes at 3000rpm to emulsify and disperse it. Furthermore, 9.4 parts by weight of a thickening solution containing 0.2 parts by weight of thickening agent (aluminium magnesium silicate), 0.1 parts by weight of thickening agent (xanthane gum) and 0.2 parts by weight of preservative additives (1,2-benzisothiazoline-3-one) is added to obtained oil-in-water emulsion, and further, 4 parts by weight of water is added

30 to make a total amount of the composition 4.

Comparative Manufacturing example 1

Comparative Composition 1 was obtained by preparing similarly to Manufacturing example 1 except that 0.55 parts by weight of stabilizer (epoxidised soybean oil) of Manufacturing example 1 was not added, and further, that 9.45 parts by weight of aromatic hydrocarbon solvent was changed into 10 parts by weight of aromatic hydrocarbon solvent.

Comparative Manufacturing example 2

Comparative Composition 2 was obtained by preparing similarly to Manufacturing example 1 except that 2.25 parts by weight of vapour retardant additive A (cetyl alcohol), 0.75 parts by weight of vapour retardant additive B (mixture of stearic acid and palmitic acid) was not added, and further, that 9.45 parts by weight of aromatic hydrocarbon solvent was changed into 12.45 parts by weight of aromatic hydrocarbon solvent.

Comparative Study 1

The following study evaluates the role of stabilizer and dispersing agent toward the stability of the end product, in particular a proposed formulation for spraying, FO-12039 ("Composition 1") which comprises stabilizer and dispersing agent. Three variations on the recipe for FO-12039 ("Composition 1") were prepared, namely:

- FI-12292 with no stabilizer;
- FI-12293 with no dispersing agent; and
- FI-12294 with no stabilizer and no dispersing agent.

Commercial standards Aqua Resigen EW and Aqua K-Othrine EW were included in the study as control formulations for comparison.

FI-12292, FI-12293 and FI-12294 were prepared with the following recipes:

Recipe	% w/w	FI-12292 (No stabilizer)	FI-12293 (No dispersing agent)	FI-12294 (No stabilizer and dispersing agent)
<u>Oil Phase</u>				
SumiOne TG (95.8%) Lot: 090301	0.1044 0.1 (pure)	1.0440 g	1.0440 g	1.0440 g
Gokilaht-S TG (95.2%) Lot: 080107	6.3025 6.0 (pure)	63.03 g	63.03 g	63.03 g

Piperonyl butoxide TG (94.6%) Lot: S8294320001	10.5708 10.0 (pure)	105.71 g	105.71 g	105.71 g
Cetyl alcohol Lot: M 112940090	2.25	22.50 g	22.50 g	22.50 g
Edenor ST 1 MY BD (mixture of stearic acid and palmitic acid) Lot: M 10029013N	0.75	7.50 g	7.50 g	7.50 g
Solvesso 200 Lot: SG 18120034	9.45 / balance	100.00 g	94.50 g	100.00 g
Amepon SB/65 Lot: L1070211	0.55	N/A	5.50 g	N/A
Genapol 0 200 Lot: DEG4101459	0.60	6.00 g	6.00 g	6.00 g
Brij S20-PA-(SG) Lot: 23844	0.46	4.60 g	4.60 g	4.60 g
Brij 010-SS-(RB) Lot: 0000558710	0.94	9.40 g	9.40 g	9.40 g
Sub total	31.98	319.78 g	319.78 g	319.78 g

Recipe	% w/w	FI-12292 (No stabilizer)	FI-12293 (No dispersing agent)	FI-12294 (No stabilizer and dispersing agent)
<u>Aqueous phase</u>				
Antifoam C emulsion Lot: 0002209125	0.10	1.00 g	1.00 g	1.00 g
Purified water	47.00 / balance	470.00 g	485.00 g	485.00 g
Gohsenol GL-05 Lot: 0233	1.50	15.00 g	N/A	N/A
Subtotal	48.60	486.00 g	486.00 g	486.00 g

Recipe	% w/w	FI-12292 (No stabilizer)	FI-12293 (No dispersing agent)	FI-12294 (No stabilizer and dispersing agent)
<u>Thickening Solution</u>				
Proxel GXL (S) Lot: T1J071	0.20	2.00 g	2.00 g	2.00 g
Purified water	14.00	140.00 g	140.00 g	140.00 g
Veegum G Lot: 2010371144	0.15	1.50 g	1.50 g	1.50 g
Kelzan S Lot: 0198661	0.075	0.75 g	0.75 g	0.75 g
Subtotal	14.425	144.25 g	144.25 g	144.25 g
<u>Water for rinsing</u>				
Purified water	4.995 (Balance)	49.95 g	49.95 g	49.95 g

Total	100.00	1000.00 g	1000.00 g	1000.00 g
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FI-12292, FI-12293 and FI-12294 were prepared using the following steps:

a) Preparation of oil phase

- 5 i) Oil phase was prepared by weighing SumiOne TG, Gokilaht-S TG, piperonyl butoxide TG, solvent, emulsifiers and stabilizer (if any, Amepon SB/65) into a container.
- ii) Next, the container was heated at 60°C.
- 10 iii) Cetyl alcohol and Edenor ST 1 MY BD (mixture of stearic acid and palmitic acid) were added gradually into the oil mixture under constant stirring.
- iv) Stirring was proceeded for ~20 minutes until all items were fully dissolved.
- v) The solution was cooled down to room temperature.

b) Preparation of aqueous phase

- 15 i) Antifoam C emulsion was weighed into the container followed by purified water.
- ii) The solution was then stirred at room temperature.
- 20 iii) Gohsenol GL-05 (if any) was added gradually into the aqueous phase under constant stirring. Stirring was proceeded for approximately ~10 minutes at room temperature until all Gohsenol GL-05 particles were uniformly distributed.
- iv) The container was heated at 60°C.
- v) The solution was then cooled down to room temperature.

c) Preparation of thickening solution

- 25 i) Proxel GXL(S) was weighed into the container followed by purified water.
- ii) The solution was then stirred using laboratory stirrer at room temperature.
- 30 iii) Veegum G was added gradually into the aqueous phase under constant stirring. Next, Kelzan S was added into the same solution. Stirring was proceeded for approximately ~10 minutes at room temperature until all solid particles were uniformly distributed.
- iv) The container was heated at 60°C.
- v) The solution was then cooled down to room temperature.

35 d) Homogenising& final mixing

- i) Under high shear mixing using TK Robomic Type A homogenizer (Premix), the oil phase was added slowly into the Gohsenol GL-05 solution.
- 40 ii) Homogenising speed was set at 7,000 rpm.
- iii) Lastly, thickening solution was added into the emulsion and stirred using laboratory stirrer at room temperature for ~20 minutes to form homogenous oil in water emulsion.

The following tests were carried out:

- a) Particle size / VMD of finished products – This measurement could be conducted by using Malvern Mastersizer 2000 base on the basic operational procedure..

- 5 b) Emulsion stability test - inspection of freshly homogenized samples or initial samples for any separation, sedimentation, oiling¹ or creaming² after dilution steps³, over 2 hours at $(30 \pm 2)^\circ \text{C}$, and after 72 hours at ambient conditions;

¹Oiling: The formation of a liquid phase not miscible with water, at the top or the bottom of emulsion.

- 10 ²Creaming: The formation of a layer containing a proportion of the dispersed phase higher than that in the remainder of the emulsion, at the top or the bottom of emulsion.

³Dilution steps:

- 15 - 90 mL of WHO standard water⁴ was poured into a 100 mL measuring cylinder with stopper. The cylinder was then immersed in water bath maintained at $(30 \pm 2)^\circ \text{C}$ for 1 hour;
 - 10 mL of the space spray EW was added into the cylinder drop wise using a measuring pipette;
 - The cylinder was stopped and inverted for 20 times continuously;
 20 - The cylinder was then re-immersed into the water bath for 2 hours at $(30 \pm 2)^\circ \text{C}$; and
 - Any oiling¹, creaming², separation or sedimentation was observed after 2 hours and again after 72 hours.

- 25 ⁴WHO Standard water: Two types as below:

- WHO standard hard water:
 0.304 g of anhydrous calcium chloride and 0.139 g of magnesium chloride hexahydrate dissolved in distilled water and made up to 1 Litre. This provides water with a hardness of 342 mg/L calculated as calcium carbonate
 30
 - WHO standard soft water:
 One part of the WHO standard hard water diluted with nine parts of distilled water to give 34.2 mg/L hardness.

- 35 c) Separation rate and active content test - If there is separation, total sample height and the height of each layer were measured to calculate the separation rate. Layers were isolated using a needle syringe and analysed for active content in order to check on uniformity after separation.

Results and Discussion:

a) Emulsion stability test

Samples	Over 2 hours dilution in 30°C water bath		Over 72 hours (3 days) dilution under ambient room conditions	
	WHO Standard Hard Water	WHO Standard Soft Water	WHO Standard Hard Water	WHO Standard Soft Water
FI-12292 (No stabilizer)	Stable emulsion	Stable emulsion	Stable emulsion	Stable emulsion
FI-12293 (No dispersing agent)	Stable emulsion	Stable emulsion	2 mL oiling on the surface	2 mL oiling on the surface
FI-12294 (No stabilizer & dispersing agent)	Stable emulsion	Stable emulsion	3 mL oiling on the surface	3 mL oiling on the surface
FO-12039 ("Composition 1") (with stabilizer and dispersing agent)	Stable emulsion	Stable emulsion	Stable emulsion	Stable emulsion
FO-12064 (Aqua Resigen EW)	Stable emulsion	Stable emulsion	1 mL creaming on the surface	1 mL creaming on the surface
FO-12065 (Aqua K-Othrine EW)	Stable emulsion	Stable emulsion	2 mL creaming on the surface	2 mL creaming on the surface

5 All fresh formulations appeared as whitish viscous liquid. Upon dispersion into WHO standard waters at ratio 1: 9, all formulations formed stable emulsions over the first 2 hours.

10 At 72 hours after dilution, formulations without the dispersing agent (FI-12293 & FI-12294) and both commercial standards, had noticeable oiling or creaming. Proposed formulation FO-12039 ("Composition 1") and formulation FI-12292 (without stabilizer but having dispersing agent) remained stable.

b) Separation rate and active content test

For the separation rate study, each formulation was well mixed, then packed into 100-mL clear glass bottle (3 bottles for each sample) and stored under the conditions of 54, 40, ambient room temperature (i.e. $(30 \pm 2)^{\circ}\text{C}$) and -5°C .

15 The samples were retrieved weekly and checked on the following parameters:

i) Physical appearance & separation rate

Aqua K-Othrine EW

Interval / Storage Conditions	54°C	40°C	RT	-5°C
Initial	Whitish liquid	Whitish liquid	Whitish liquid	Whitish liquid
1 week	Oiling on surface, separated into 2 layers: - top layer 12% height, yellower tone - bottom layer 88% height, lighter tone	Oiling on surface, separated into 2 layers: - top layer 36% height, yellower tone - bottom layer 64% height, lighter tone	Separated into 2 layers: - top layer 54% height, yellower tone - bottom layer 46% height, lighter tone	No separation
2 weeks	Oiling on surface, separated into 3 layers: - top layer 12% height, yellower tone - middle layer 81% height - bottom layer 7% height, lighter tone	Oiling on surface, separated into 2 layers: - top layer 40% height, yellower tone - bottom layer 60% height, lighter tone	Separated into 2 layers: - top layer 54% height, yellower tone - bottom layer 46% height, lighter tone	No separation
3 weeks	Oiling on surface, separated into 3 layers: - top layer 49% height, yellower tone - middle layer 42% height, whitish - bottom layer 9% height, lighter tone	Oiling on surface, separated into 2 layers: - top layer 40% height, yellower tone - bottom layer 60% height, lighter tone	Separated into 2 layers: - top layer 51% height, yellower tone - bottom layer 49% height, lighter tone	No separation
4 weeks	Oiling on surface, separated into 3 layers: - top layer 26% height, yellower tone - middle layer 60% height, whitish - bottom layer 14% height, lighter tone	Oiling on surface, separated into 2 layers: - top layer 40% height, yellower tone - bottom layer 60% height, lighter tone	Separated into 2 layers: - top layer 51% height, yellower tone - bottom layer 49% height, lighter tone	No separation

Aqua Resigen EW

Interval/ Storage	54°C	40°C	RT	-5°C
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Initial	Whitish liquid	Whitish liquid	Whitish liquid	Whitish liquid
1 week	Oiling on surface, separated into 2 layers: - top layer 93% height, yellower tone - bottom layer 7% height, semi translucent tone	Oiling on surface, separated into 2 layers: - top layer 93% height, yellower tone - bottom layer 7% height, semi translucent tone	Separated into 2 layers: - top layer 97% height, yellower tone - bottom layer 3% height, semi translucent tone	No separation
2 weeks	Oiling on surface, separated into 2 layers: - top layer 81% height, yellower tone - bottom layer 19% height, semi translucent tone	Oiling on surface, separated into 2 layers: - top layer 90% height, yellower tone - bottom layer 10% height, semi translucent tone	Separated into 2 layers: - top layer 97% height, yellower tone - bottom layer 3% height, semi translucent tone	No separation
3 weeks	Oiling on surface, 3 layers: - top layer 43% height, yellower tone - middle layer 33% height - bottom layer 24% height, semi translucent tone	Oiling on surface, 3 layers: - top layer 15% height, yellower tone - middle layer 70% height - bottom layer 15% height, semi translucent tone	Separated into 2 layers: - top layer 93% height, yellower tone - bottom layer 7% height, semi translucent tone	No separation
4 weeks	Oiling on surface, 4 layers: - top layer 21% height, yellower tone - 2nd layer 49% height - 3rd layer 24% height - bottom layer 6% height, semi translucent tone	Oiling on surface, 3 layers: - top layer 14% height, yellower tone - middle layer 72% height - bottom layer 14% height, semi translucent tone	Separated into 2 layers: - top layer 92% height, yellower tone - bottom layer 8% height, semi translucent tone	No separation

FO-12039 ("Composition 1")

Interval / Storage	54°C	40°C	RT	-5°C
Initial	Whitish liquid	Whitish liquid	Whitish liquid	Whitish liquid
1 week	No separation	No separation	No separation	No separation
2 weeks	Minor oiling on surface, no separation	Minor oiling on surface, no separation	No separation	No separation
3 weeks	Minor oiling on surface, no separation	Minor oiling on surface, no separation	No separation	No separation
4 weeks	Minor oiling on surface, no separation	Minor oiling on surface, no separation	No separation	No separation

FI-12292(without stabilizer)

Interval / Storage	54°C	40°C	RT	-5°C
Initial	Whitish liquid	Whitish liquid	Whitish liquid	Whitish liquid
1 week	No separation	No separation	No separation	No separation
2 weeks	Minor oiling on surface, no separation	Minor oiling on surface, no separation	No separation	No separation
3 weeks	Minor oiling on surface, no separation	Minor oiling on surface, no separation	No separation	No separation
4 weeks	Minor oiling on surface, no separation	Minor oiling on surface, no separation	No separation	No separation

5 FI-12293(without dispersing agent)

Interval / Storage conditions	54°C	40°C	RT	-5°C
Initial	Whitish liquid	Whitish liquid	Whitish liquid	Whitish liquid
1 week	Sedimentation, 6% height at base level	No separation	No separation	No separation
2 weeks	Minor oiling on surface. Sedimentation, 6% height at base level	Minor oiling on surface, no separation	No separation	No separation

3 weeks	Minor oiling on surface. Sedimentation, 6% height at base level.	Minor oiling on surface, no separation	No separation	No separation
4 weeks	Minor oiling on surface. Sedimentation, 7% height at base level.	Minor oiling on surface, no separation	No separation	No separation

FI-12294(without stabiliser and dispersing agent)

Interval / Storage conditions	54°C	40°C	RT	-5°C
Initial	Whitish liquid	Whitish liquid	Whitish liquid	Whitish liquid
1 week	Sedimentation, 7% height at base	No separation	No separation	No separation
2 weeks	Minor oiling on surface. Sedimentation, 7% height at base.	Minor oiling on surface, no separation	No separation	No separation
3 weeks	Minor oiling on surface. Sedimentation, 7% height at base.	Minor oiling on surface, no separation	No separation	No separation
4 weeks	Minor oiling on surface. Sedimentation, 8% height at base.	Minor oiling on surface, no separation	No separation	No separation

From the study, it was seen that both commercial products from Bayer (Aqua K-Othrine
5 EW & Aqua Resigen EW) separated under ambient room conditions and high temperature storage. However, Composition 1 remained stable with no separation.

ii) Particle size of finished product

Aqua K-Othrine EW

Testing	-5°C	RT	40°C	54°C
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Interval	Single Layer (No separation)	TOP	BOTTOM	TOP	BOTTOM	TOP	MIDDLE	BOTTOM
Initial	1.2 μm	1.2 μm		1.2 μm		1.2 μm		
1 st Week	1.1 μm	1.5 μm	0.48 μm	1.8 μm	0.57 μm	2.5 μm	-	1.1 μm
2 nd Week	1.2 μm	1.6 μm	0.44 μm	1.8 μm	0.52 μm	2.9 μm	0.97 μm	0.54 μm
3 rd Week	1.1 μm	1.4 μm	0.46 μm	2.1 μm	0.59 μm	2.8 μm	0.74 μm	0.48 μm
4 th Week	1.0 μm	1.5 μm	0.47 μm	1.9 μm	0.56 μm	3.5 μm	0.68 μm	0.47 μm

Note: For 1st week sample under 54°C storage, 2 layers of separation were noticeable. For the following weeks (3rd week onwards), 3 layers of separation were observed.

Aqua Resigen EW

Testing Interval	-5°C	RT		40°C ^{#2}			54°C ^{#3}			
	No Separation	TOP	BOTTOM	TOP	MIDDLE	BOTTOM	1 st LAYER	2 nd LAYER	3 rd LAYER	4 th layer (BOTTOM)
Initial	3.4 μm	3.4 μm		3.4 μm			3.4 μm			
1 st Week	3.5 μm	Not tested	Not tested	Not tested	-	Not tested	5.5 μm	-	-	0.74 μm
2 nd Week	3.4 μm	5.9 μm	0.99 μm	6.5 μm	-	0.61 μm	5.6 μm	-	-	0.59 μm
3 rd Week	3.3 μm	5.3 μm	0.91 μm	6.4 μm	1.5 μm	0.60 μm	5.2 μm	1.0 μm		0.68 μm
4 th Week	3.2 μm	4.0 μm	0.77 μm	5.6 μm	1.3 μm	0.56 μm	5.5 μm	1.5 μm	0.77 μm	0.67 μm

5 FO-12039 ("Composition 1")

Testing Interval	-5°C	RT	40°C	54°C
Initial	0.62 μm	0.62 μm	0.62 μm	0.62 μm
1 st Week	0.63 μm	Not tested	Not tested	0.63 μm
2 nd Week	0.62 μm	0.62 μm	0.62 μm	0.64 μm
3 rd Week	0.63 μm	0.62 μm	0.62 μm	0.63 μm
4 th Week	0.62 μm	0.62 μm	0.61 μm	0.63 μm

FI-12292(without stabilizer))

Testing Interval	-5°C	RT	40°C	54°C
Initial	0.74 µm	0.74 µm	0.74 µm	0.74 µm
1st Week	1.1µm	Not tested	Not tested	1.1 µm
2nd Week	1.1 µm	1.23 µm	1.3 µm	1.1 µm
3rd Week	1.2 µm	1.2 µm	1.2 µm	1.1 µm
4th Week	1.2 µm	1.2µm	1.2 µm	1.2 µm

FI-12293(without dispersing agent)

Testing Interval	-5°C	RT	40°C	54°C
Initial	1.5 µm	1.5 µm	1.5 µm	1.5 µm
1st Week	1.4 µm	Not tested	Not tested	1.5 µm
2nd Week	1.5 µm	1.5 µm	1.6 µm	1.5 µm
3rd Week	1.5 µm	1.5 µm	1.5 µm	1.7 µm
4th Week	1.5 µm	1.5 µm	1.5 µm	1.5 µm

FI-12294(without stabiliser and dispersing agent)

Testing Interval	-5°C	RT	40°C	54°C
Initial	1.4 µm	1.4 µm	1.4 µm	1.4 µm
1st Week	1.6 µm	Not tested	Not tested	1.7 µm
2nd Week	1.7 µm	1.8 µm	1.9 µm	1.7 µm
3rd Week	1.7 µm	1.8 µm	1.8 µm	1.7 µm
4th Week	1.8 µm	1.8 µm	1.7 µm	1.7 µm

5

Particle sizes for the Bayer commercial standard products were larger compared to the particle size of Composition 1. On separation (for Aqua K-Othrine EW & Aqua Resigen EW), the particle size of each layer was also significantly different, i.e the top layer particles were larger than the middle or bottom layer particles. Under high temperature storage, the particles of Aqua K-Othrine EW & Aqua Resigen EW tended to increase in size but the Manufacturing expample1 remained stable, with no increase or decrease in its particle size under all storage conditions.

10

From the above results, we can see that the formulation droplets in samples with no stabilizer grew to around twice the size. Accordingly, the presence of a stabiliser (Amepon SB/65) is essential to minimise the increase in particle size. As seen previously, the presence of dispersing agent (Gohsenol GL-05) in the formulation helped
5 to achieve a small particle size of less than 1 μm . The presence of a dispersing agent (Gohsenol GL-05) is necessary to obtain the size of fine particles (less than 1 μm).

iii) Active ingredients content of each layer upon separation.

Product / storage condition	Layer	Analysed active content (% w/w)	Difference against stated content (%)	Stated active content (% w/w)
FO-12039 ("Composition 1")	Top portion (1/4 height from surface)	SumiOne: 0.102 Gokilaht-S: 5.96 Piperonyl butoxide: 10.07	No significant different from stated active Content	SumiOne: 0.1 Gokilaht-S: 6 Piperonyl butoxide: 10
	Bottom portion (1/4 height from base)	SumiOne: 0.102 Gokilaht-S: 5.92 Piperonylbutoxide: 9.96	No significant different from stated active content	
Aqua K-Othrine EW (ambient room temperature, 2 weeks)	Top layer Bottom layer	Deltamethrin: 3.61 Deltamethrin: 0.35	Higher by 81% Less by 83%	Deltamethrin: 2% w/w
Aqua Resigen EW (ambient room temperature, 4 weeks)	Top layer	S-bioallethrin: 0.210 Permethrin: 16.60 Piperonyl butoxide: 16.39	S-bioallethrin: higher by 50% Permethrin: higher by 64% Piperonyl butoxide: higher by 65%	S-bioallethrin: 0.14 Permethrin: 10.11 Piperonyl butoxide: 9.96
	Bottom layer	S-bioallethrin: 0.025 Permethrin: 2.00 Piperonyl butoxide: 2.00	S-bioallethrin: less by 82% Permethrin: less by 80% Piperonyl butoxide: less by 80%	
Aqua Resigen EW (54°C, 2 weeks)	Top layer	S-bioallethrin: 0.220 Permethrin: 17.36 Piperonyl butoxide: 16.97	S-bioallethrin: higher by 57% Permethrin: higher by 72% Piperonyl butoxide: higher by 70%	S-bioallethrin: 0.14 Permethrin: 10.11 Piperonyl butoxide: 9.96
	Bottom layer	S-bioallethrin: 0.014 Permethrin: 1.04 Piperonyl butoxide: 1.06	S-bioallethrin: less by 90% Permethrin: less by 90% Piperonyl butoxide: less by 89%	

Aqua Resigen EW (54°C, 4 weeks)	Top (1 st) layer	S-bioallethrin: 0.240 Permethrin: 20.08 Piperonyl butoxide: 19.37	S-bioallethrin: higher by 71% Permethrin: higher by 99% Piperonyl butoxide: higher by 70%	S-bioallethrin: 0.14 Permethrin: 10.11 Piperonyl butoxide: 9.96
	2 nd layer	S-bioallethrin: 0.090 Permethrin: 7.40 Piperonyl butoxide: 7.20	S-bioallethrin: less by 36% Permethrin: less by 27% Piperonyl butoxide: less by 28%	
	3 rd layer	S-bioallethrin: 0.034 Permethrin: 2.75 Piperonyl butoxide: 2.68	S-bioallethrin: less by 76% Permethrin: less by 73% Piperonyl butoxide: less by 73%	
	Bottom (4 th) layer	S-bioallethrin: 0.008 Permethrin: 0.68 Piperonyl butoxide: 0.67	S-bioallethrin: less by 94% Permethrin: less by 93% Piperonyl butoxide: less by 93%	

From the active ingredient content analysis, it was found that the deltamethrin content in Aqua K-Othrine EW was not homogeneous throughout the container when the formulation separated. The active content in the bottom layer was 83% lower than the stated content. The same issue was observed for Aqua Resigen EW where higher active contents were observed in the top layer compared to the middle and bottom layers. However, the active content of the Composition 1 remained uniform.

As may be seen from the above, the presence of stabilizer and dispersing agent improves the stability of a spray formulation. There are benefits to having a stable formulation versus an unstable (separated) formulation. In an unstable formulation that separates into layers, the active ingredient is not evenly distributed throughout the formulation. Due to the separation and lack of uniformity of active ingredient, the end user must shake the product well before use. Failure to ensure good homogeneity before use will affect the efficacy of the product. On the other hand, if the product does not separate to any serious extent, there is less need for the bottle to be shaken before use, and less chance of application dosing errors coming in to play.

CLAIMS

1. A formulation suitable for spraying comprising an oil phase comprising at least one active ingredient, a stabiliser, a vapour retardant additive, and optionally at least one emulsifier, wherein:
 - the stabiliser comprises at least one epoxidised vegetable oil; and
 - the vapour retardant additive is selected from the group consisting of one or more of cetyl alcohol, stearic acid and palmitic acid.
2. The formulation according to claim 1, further comprising an aqueous phase comprising at least one dispersing agent.
3. The formulation according to claim 2, further comprising at least one selected from the group consisting of antifoam agents and thickening agents.
4. The formulation according to any one of the preceding claims, wherein the at least one epoxidised vegetable oil is derived from at least one vegetable oil selected from the group consisting of soybean oil, Jatropha oil, linseed oil, neem oil, palm oil, coconut oil, cottonseed oil, peanut oil, olive oil, rapeseed oil, safflower oil, sesame oil, sunflower oil, almond oil, beechnut oil, cashew oil, hazelnut oil, macadamia oil, mongongo oil, pecan oil, pine nut oil, pistachio oil, and walnut oil.
5. The formulation according to any one of the preceding claims, wherein the stabiliser is epoxidised soybean oil.
6. The formulation according to any one of the preceding claims, wherein the active ingredient is at least one selected from the group consisting of an insecticide, herbicide, fungicide, acaricide, insect repellent, deodoriser and drug.
7. The formulation according to any one of the preceding claims, wherein the active ingredient comprises at least one pyrethroid compound.
8. The formulation according to claim 7, wherein the pyrethroid compound is selected from the group consisting of allethrin, phalthrin, prallethrin, furamethrin, empenethrin, phenothrin, permethrin, cyphenothrin, cypermethrin, decamethrin, tralomethrin, deltamethrin, bifenthrin, cyfluthrin, etofenprox, transfluthrin, cycloprothrin, acrinathrin, fenvalerate, esfenvalerate, flucythrinate, tefluthrin,

esbiothrin, fenpropathrin, tetramethrin, fluvalinate, cyhalothrin, resmethrin, meperfluthrin, teflumethrin, dimefluthrin, Pyrethrin I, Pyrethrin II, Cinerin I, Cinerin II, jasmolin I, jasmolin II and metofluthrin.

9. The formulation according to any one of the preceding claims, wherein the at least one active ingredient comprises cyphenothrin and/or metofluthrin and optionally piperonyl butoxide.
10. A spray container comprising the formulation according to any one of the preceding claims.
11. A method of preparing a formulation suitable for spraying, comprising preparing an oil phase comprising at least one active ingredient, a stabiliser, a vapour retardant additive, and optionally at least one emulsifier, wherein:
 - the stabiliser comprises at least one epoxidised vegetable oil; and
 - the vapour retardant additive is selected from the group consisting of one or more of cetyl alcohol, stearic acid and palmitic acid.
12. The method according to claim 11, further comprising adding an aqueous phase comprising at least one dispersing agent and optionally at least one antifoam agent and/or thickening agent.
13. The method according to any one claims 11 to 12, wherein the at least one epoxidised vegetable oil is derived from at least one vegetable oil selected from the group consisting of soybean oil, Jatropha oil, lindseed oil, neem oil, palm oil, coconut oil, cottonseed oil, peanut oil, olive oil, rapeseed oil, safflower oil, sesame oil, sunflower oil, almond oil, beechnut oil, cashew oil, hazelnut oil, macadamia oil, mongongo oil, pecan oil, pine nut oil, pistachio oil, and walnut oil.
14. The method according to any one of claims 11 to 13, wherein the stabiliser is epoxidised soybean oil.
15. The method according to any one of claims 11 to 14, wherein the active ingredient is at least one selected from the group consisting of an insecticide, herbicide, fungicide, acaricide, insect repellent, deodoriser and drug.

16. The method according to any one of claims 11 to 15, wherein the active ingredient comprises at least one pyrethroid.
17. The method according to claim 16, wherein the pyrethroid compound is selected from the group consisting of allethrin, phtalthrin, prallethrin, furamethrin, empenethrin, phenothrin, permethrin, cyphenothrin, cypermethrin, decamethrin, tralomethrin, deltamethrin, bifenthrin, cyfluthrin, etofenprox, transfluthrin, cycloprothrin, acrinathrin, fenvalerate, esfenvalerate, flucythrinate, tefluthrin, esbiothrin, fenpropathrin, tetramethrin, fluvalinate, cyhalothrin, resmethrin, meperfluthrin, teflumethrin, dimefluthrin, Pyrethrin I, Pyrethrin II, Cinerin I, Cinerin II, jasmolin I, jasmolin II and metofluthrin.
18. The method according to any one of claims 11 to 17, wherein the formulation comprises cyphenothrin and/or metofluthrin and optionally piperonyl butoxide.
19. Use of the formulation according to any one of claims 1 to 9, optionally diluted with water, or the spray container according to claim 10, to control insects, acarine pests or unwanted plants.