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(54) Title: WATER-SUSPENDABLE AGRICULTURAL CHEMICAL COMPOSITION

(57) Abstract: The present invention relates to a stable, water-suspendable agricultural chemical composition comprising at least one liquid agricultural chemical ingredient, at least one solid agricultural chemical ingredient, at least one oil and at least one poly-ol comprising at least 3 hydroxyl groups, which is able to reduce contact phytotoxicity on crops of useful plants, especially on rice crops.



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Water-suspendable agricultural chemical composition

The present invention relates to a stable, water-suspendable agricultural chemical composition, which is able to reduce contact phytotoxicity on crops of useful plants, especially on rice crops. The present invention also relates to a method of controlling undesired vegetation in crops of useful plants, especially in rice crops, as well as the use of said composition for controlling grasses and weeds in crops of useful plants, especially in rice crops.

The formulations according to the instant invention comprise blends of two or more types of active ingredients having different physical properties. They are designed in order to avoid hydrolysis, precipitation and aggregation of all active ingredients while ensuring adequate dispersion, suspension, emulsification or combinations thereof of the active ingredients.

However, despite showing a good stability since hydrolysis, precipitation and aggregation are inhibited, even when stored for a long period of time, aqueous liquid compositions comprising pretilachlor, a chloroacetamide herbicide, bensulfuron-methyl, a sulfonylurea herbicide, pyriftalid, a pyrimidinyloxybenzoate-based herbicide, an oily phase, at least one antifreeze agent, at least one surfactant, a biocide, a pH regulator, a thickening agent and an antifoam agent show an unexpected contact phytotoxicity on the crops of useful plants, especially on rice leaves.

As a result of conducting extensive studies that focused on the aforementioned problems, the inventors of the present invention found that the origin of the contact phytotoxicity on rice leaves is essentially caused by the presence of pretilachlor. The inventors also found that the presence in said formulations of liquid paraffin as oily phase, and of propylene glycol as antifreeze agent increased the phytotoxicity of pretilachlor by their synergetic effect.

Surprisingly, the aforementioned problems are solved by using as antifreeze agents at least one poly-ol compound comprising at least three hydroxyl groups instead of propylene glycol which contains only two hydroxyl groups, and by using soybean oil instead of liquid paraffin as oily phase, thereby leading to completion of the present invention. Soybean oil

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surprisingly, does not show the above-mentioned negative synergetic effect of liquid paraffin on pretilachlor in the oily phase. Likewise, the use of glycerol, which contains three hydroxyl groups or of polyvinyl alcohol, which contains more than three hydroxyl groups, as antifreeze agent, instead of propylene glycol (propan-1,2-diol), which contains only two hydroxyl groups
5 strongly reduces the contact injury of pretilachlor on rice leaves and lead to an unexpected safening effect. On the other hand, the use of ethylene glycol (ethan-1,2-diol), which contains only two hydroxyl groups, as antifreeze agent lead to a strong contact injury on rice leaves.

10 Thus, the present application includes the following inventions.

In a first aspect, the present invention provides a water-suspendable agricultural chemical composition comprising at least one liquid agricultural chemical ingredient, at least one solid agricultural chemical ingredient, at least one oil and at least one poly-ol compound
15 comprising at least 3 hydroxyl groups.

In a first embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the oil is selected from the group consisting of mineral oil, vegetable oil, fatty acid ester, epoxidized vegetable oil and liquid paraffin.

20 In a second embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the oil is a vegetable oil.

In a third embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the vegetable oil is soybean oil.
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In a fourth embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the poly-ol compound is glycerol.

30 In a fifth embodiment, the present invention provides a water-suspendable agricultural chemical composition comprising at least one nonionic surfactant.

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In a sixth embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the nonionic surfactant is polyoxyethylene-polyoxypropylene block polymer.

5 In a seventh embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the liquid or solid agricultural chemical ingredient is at least one herbicide.

10 In an eighth embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the liquid or solid agricultural chemical ingredient is at least one insecticide.

15 In a ninth embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the liquid or solid agricultural chemical ingredient is at least one bactericide.

20 In a tenth embodiment, the present invention provides a water-suspendable agricultural chemical composition comprising at least one bactericide and at least one insecticide as agricultural chemical ingredients.

In an eleventh embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein at least one of the liquid agricultural chemical ingredients is a chloroacetamide-based herbicide.

25 In a twelfth embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the chloroacetamide-based herbicide is pretilachlor.

30 In a thirteenth embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the solid agricultural chemical ingredient is a sulfonylurea-based herbicide.

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In a fourteenth embodiment, the present invention provides a water-suspendable agricultural chemical composition wherein the sulfonylurea-based herbicide is bensulfuron-methyl.

5 In a fifteenth embodiment, the present invention provides a water-suspendable agricultural chemical composition that further comprises pyriftalid, a pyrimidinyloxybenzoate-based herbicide as a solid agricultural chemical ingredient.

10 In a second aspect, the present invention provides a method of controlling undesired vegetation in crops of useful plants, especially in rice crops, which comprises allowing an effective amount of the water-suspendable agricultural chemical composition to act where control is desired.

15 In a third aspect, the present invention provides the use of the water-suspendable agricultural chemical composition for controlling grasses and weeds in crops of useful plants, especially in rice crops.

20 In a fourth aspect, the present invention provides a method for the preparation of the agricultural chemical composition according to the present invention by blending an oil into a water-suspendable agricultural chemical composition comprising at least one liquid agricultural chemical ingredient and at least one solid agricultural chemical ingredient.

25 In a fifth aspect, the present invention provides a use of at least one poly-ol comprising at least 3 hydroxyl groups in compositions according to the instant invention to reduce the contact injury of pretilachlor on leaves of crops of useful plants.

30 In an embodiment, the present invention provides the use of glycerol as poly-ol comprising at least 3 hydroxyl groups to reduce the contact injury of pretilachlor on leaves of crops of useful plants.

In another embodiment, the present invention provides the use of at least one poly-ol, especially glycerol, in admixture with soybean oil in compositions according to the instant invention to reduce the contact injury of pretilachlor on leaves of crops of useful plants, especially in rice crops.

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The present invention provides a water-suspendable agricultural chemical composition comprising at least one liquid agricultural chemical ingredient, at least one solid agricultural chemical ingredient, at least one oil and at least one poly-ol antifreeze agent comprising at least three hydroxyl groups, for which satisfactory dispersion, suspension, emulsification or combinations thereof of the contained ingredients are secured, hydrolysis, precipitation and aggregation are also inhibited, even if stored for a long period of time.

There are no particular limitations on liquid agricultural chemical ingredients that can be used in the water-suspendable agricultural chemical composition as claimed in the present invention provided they are agricultural chemical ingredients in a vitreous, oily or liquid state at normal temperature and normal pressure such as the temperature during composition production, in a composition or in a sprayed liquid, or depending on the particular case, at a temperature up to about 50°C. Typical examples include chloroacetamide-based compounds such as pretilachlor, carbamate-based compounds and dinitroaniline-based compounds. In addition, ingredients that are in an oily state at the purity at which they are normally used in agricultural chemical compositions are also included in the liquid agricultural chemical ingredients of the present invention even if they are a solid at room temperature when in the pure form. Agricultural chemical ingredients may be, for example, herbicides, bactericides, fungicides, nematocides, parasitocides or other biocides. Liquid agricultural chemical ingredients are preferably herbicides, insecticides, bactericides or insecticide/fungicides, and particularly preferably herbicides.

Examples of liquid herbicides include, but are not limited to, pretilachlor (656), metolachlor (548), prodiamine (661), esprocarb (303), prosulfocarb (683), triclopyr (827), fluazifop (681), orbencarb (595), molinate (560), dimetnamide (260), pelargonic acid (583), dalapon (214), piperophos (560), butamiphos (102), glyphosate trimesium (419), sethoxydim (726), clethodim (153), S-metolachlor (549) and cinmethylin (153). In the present invention, the chloroacetamide-based herbicides pretilachlor (656) and metolachlor (548) are preferable, with pretilachlor being particularly preferable. These compounds and agronomically acceptable salts thereof are described, for example, in "The e-Pesticide Manual", version 3.1, 13th Edition, Ed. CDC Tomlin, British Crop Protection Council, 2004-2005.

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Examples of liquid insecticides include, but are not limited to, cyanophos (184), fenthion (346), fenitrothion (335), dichlofenthion (1051), pirimiphos-methyl (1345), diazinon (227), isoxathion (480), oxydeprofos (1324), marathion, phenthoate (631), formothion (1192), thiometon (801), disulfoton (278), prothiophos (686), sulprofos (1408), propenofos, pyraclofos (689), dichlorvos (236), naled (657), chlorfenvinphos (131), propaphos (1356), isofenphos (1236), ethion (309), carbosulfan (119), benfuracarb (60), allethrin (17), permethrin (626), cyhalothrin (196), cyfluthrin (193), fenvalerate (349), flucythrinate (367), fluvalinate (1184), cycloprothrin (188), silafluofen (728), propargite (671), halfenprox (424), ethoprophos (312) and fosthiazate (408). These compounds and agronomically acceptable salts thereof are described, for example, in "The e-Pesticide Manual", version 3.1, 13th Edition, Ed. CDC Tomlin, British Crop Protection Council, 2004-2005.

Other examples of liquid agricultural chemical ingredients include liquid bactericides, and particularly fungicides such as calcium polysulfide (111), ediphenfos (290), propiconazole (675), pefurazoate (618), pyrifeno (703), tetraconazole (778), echlomezole (321), dinocap (270) and metalaxyl M (516). These compounds and agronomically acceptable salts thereof are described, for example, in "The e-Pesticide Manual", version 3.1, 13th Edition, Ed. CDC Tomlin, British Crop Protection Council, 2004-2005.

A liquid agricultural chemical ingredient as claimed in the present invention is particularly preferably that which has low water solubility such as water solubility of 1000 mg/l or less at normal temperature and normal pressure, and preferably 500 mg/l or less. Examples of such liquid agricultural chemical ingredients include pretilachlor (water solubility: 50 mg/l), metolachlor (water solubility: 488 mg/l), prodiamine (water solubility: 0.013 mg/l), esprocarb (water solubility: 4.9 mg/l), prosulfocarb (water solubility: 13.2 mg/l) and metalaxyl M (water solubility: 26 mg/l).

The aforementioned liquid agricultural chemical ingredients are preferably blended in an amount of 0.1 to 60 parts by weight, and more preferably 5 to 40 parts by weight, based on 100 parts by weight for the total weight of the water-suspendable agricultural chemical composition as claimed in the present invention.

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There are no particular limitations on solid agricultural chemical ingredients that can be used in the water-suspendable agricultural chemical composition as claimed in the present invention provided they are agricultural chemical ingredients that are in a solid state at normal temperature and normal pressure such as the temperature during composition production, in a composition or in a sprayed liquid. Typical examples of these ingredients include sulfonylurea-based compounds. The agricultural chemical ingredients may be, for example, herbicides, insecticides, bactericides, fungicides, nematocides, parasitocides and other biocides. Liquid agricultural chemical ingredients are preferably herbicides, insecticides, bactericides or insecticide/bactericides, and particularly preferably herbicides.

Examples of solid herbicides include, but are not limited to, bensulfuron-methyl (64), CNP (974), naproanilide (517), bifenox (75), pyributicarb (698), bromobutide (93), mefenacet (505), daimuron (213), imazosulfuron (456), pyrazosulfuron-ethyl (694), simetryn (732), prometryn (666), dimethametryn (259), chlomethoxynil, oxadiazon (600), pyrazolate (692), pyrazoxyfen (695), clomeprop (160), benzofenap (70), thenylchlor (789), oxaziclomefone (604), pentoxazone (625), cafenstrole (110), azimsulfuron (43), pyriminobac-methyl (707), fentrazamide (348) and bispyribac-sodium salt (82). In the present invention, the sulfonylurea-based herbicide, bensulfuron-methyl (64), is particularly preferable. These compounds and agronomically acceptable salts thereof are described, for example, in "The e-Pesticide Manual", version 3.1, 13th Edition, Ed. CDC Tomlin, British Crop Protection Council, 2004-2005.

Examples of solid insecticides include, but are not limited to, imidacloprid (458), dinotefuran (271), thiamethoxam (792), acetamiprid (4), thiacloprid (791), nitenpyram (579), NAC (115), pyridaphenthion (701), chlorpyrifos-methyl (146), dimethoate (262), acephate (2), cartap (123), thiocyclam (798), bensultap (66) and buprofezin (99). These compounds and agronomically acceptable salts thereof are described, for example, in "The e-Pesticide Manual", version 3.1, 13th Edition, Ed. CDC Tomlin, British Crop Protection Council, 2004-2005.

Examples of solid bactericides, and particularly solid fungicides include, but are not limited to, cyprodinil (208), mepanipyrim (508), pyrimethanil (705), metalaxyl (516), mepronil (510), flutolanil (396), tecloftalam (766), pencycuron (620), diclomezine (239), triflumizole (834), kasugamycin (483), validamycin (846), probenazole (658), isoprothiolane (474),

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cyproconazole (207), metconazole (525), tricyclazole (828), pyroquilon (710), oxolinic acid (606), ferimzone (351), iprodione (470), triforine (838), picoxystrobin (647), azoxystrobin (47), kresoxim-methyl (485), orysastrobin, pyraclostrobin (690), trifloxystrobin (832) and metominostrobin (551). These compounds and agronomically acceptable salts thereof are described, for example, in "The e-Pesticide Manual", version 3.1, 13th Edition, Ed. CDC Tomlin, British Crop Protection Council, 2004-2005.

The aforementioned solid agricultural chemical ingredients are preferably blended in an amount of 0.1 to 60 parts by weight, and more preferably 0.1 to 40 parts by weight, based on 100 parts by weight for the total weight of the water-suspendable agricultural chemical composition as claimed in the present invention.

The water-suspendable agricultural chemical composition as claimed in the present invention contains at least an oil as an emulsion stabilizer for maintaining dispersivity and suspendability of liquid agricultural chemical ingredients and solid agricultural chemical ingredients, and to inhibit decomposition of solid agricultural chemical ingredients by liquid agricultural chemical ingredients. Examples of this oil include mineral oils such as spindle oil, machine oil and liquid paraffin, aromatic solvents such as Solvesso and Shellsol, vegetable oils such as rapeseed oil, soybean oil, sunflower seed oil, castor oil, pine oil and cottonseed oil, and derivatives of these oils such as methyl esters and other ester derivatives, epoxidized derivatives and fatty acid esters, and these can be used alone or in combination. Particularly preferable oil in the present invention is vegetable oil. Especially preferable vegetable oil in the present invention is soybean oil. These oils are preferably blended in an amount of 0.1 to 30 parts by weight, and more preferably 1 to 10 parts by weight, based on 100 parts by weight for the total weight of the water-suspendable agricultural chemical composition as claimed in the present invention.

In addition to each of the aforementioned ingredients, the water-suspendable agricultural chemical composition as claimed in the present invention also contains at least one antifreeze agent, which comprises at least 3 hydroxyl groups in itself, for example glycerol, polyvinyl alcohol, pentaerythrol, sugars, polysaccharides, dextrin or cellulose derivatives, preferably glycerol or polyvinyl alcohol, more preferably glycerol.

The water-suspendable agricultural chemical composition as claimed in the present invention preferably comprises at least one surfactant. Examples of preferable surfactants include polyoxyethylene-polyoxypropylene block polymer types of surfactants such as polyoxyethylene-polyoxypropylene (POE-POP) block polymer and alkyl polyoxyethylene-polyoxypropylene block polymer ether, while polyoxyethylene-polyoxypropylene (POE-POP) block polymers are particularly preferable. The use of the aforementioned surfactants is preferable because it allows a satisfactory emulsification of liquid agricultural chemical ingredients and a satisfactory dispersion of solid agricultural chemical ingredients, as well as it inhibits the decomposition of solid agricultural chemical ingredients by liquid agricultural chemical ingredients. The aforementioned surfactants are preferably blended in an amount of 0.01 to 10 parts by weight, and more preferably 0.1 to 5 parts by weight, based on 100 parts by weight for the total weight of the water-suspendable agricultural chemical composition as claimed in the present invention.

A preferable surfactant is a POE-POP block polymer, and those having an average molecular weight of 10,000 or more and an ethylene oxide weight ratio of 50% or more (such as Epan U-108, Daiichi Kogyo Seiyaku) are particularly preferable since they are able to inhibit the occurrence of aggregation under severe testing conditions. However, even those having an average molecular weight of 10,000 or less or ethylene oxide weight ratio of 50% or less are able to achieve satisfactory emulsification of liquid active ingredients and inhibit decomposition of solid active ingredients. In addition, the combined use of a plurality of POE-POP block polymers having different average molecular weights or different ethylene oxide weight ratios allows to obtain compositions having desired physical properties.

Other surfactants may also be blended into a water-suspendable agricultural chemical composition as claimed in the present invention, examples of which include nonionic surfactants such as polyoxyalkylene tristyryl phenols, polyethylene glycol higher fatty acid esters, polyoxyalkylene alkyl ethers, polyoxyalkylene alkyl aryl ethers, polyoxyalkylene aryl phenyl ethers, sorbitan alkylates, acetylene alcohols, acetylene diols and their alkylene oxide addition products, polyalkylene sorbitan alkylates, polyalkyl glycosides, sucrose fatty acid esters and polyalkylene alkyl amines, anionic surfactants such as alkyl aryl sulfonates, dialkyl sulfonates, lignin sulfonates, alkylated or non-alkylated naphthalene sulfonates and their condensation products, alkyl sulfuric acid esters and ester salts, alkyl phosphoric acid esters and ester salts, alkyl aryl sulfuric acid esters and ester salts, alkyl aryl phosphoric acid

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esters and ester salts, polyoxyethylene alkyl ether sulfuric acid esters and ester salts, polyoxyethylene alkyl aryl sulfuric acid esters and ester salts, polyoxyethylene aryl phenyl ether sulfuric acid esters and ester salts and polycarboxylic acid polymer activating agents, amphoteric surfactants such as silicone-based surfactants, fluorine-based surfactants and alkyl betaine, and cationic surfactants such as alkyl methyl ammonium salts and polyoxyalkylene alkyl methyl ammonium salts. In a preferable mode, a water-suspendable agricultural chemical composition as claimed in the present invention contains polyoxyethylene tristyryl phenol as another surfactant. This surfactant is preferably blended in an amount of 0.001 to 10 parts by weight, and more preferably 0.01 to 1 part by weight, based on 100 parts by weight for the total weight of the water-suspendable agricultural chemical composition as claimed in the present invention.

In addition to each of the aforementioned ingredients, a water-suspendable agricultural chemical composition as claimed in the present invention also contains a commonly used vehicle typically used in water-suspendable agricultural chemical compositions, examples of which include antifoaming agents such as silicone, anti-mold agents such as 1,3-benzisothiazolin-3-one and other benzisothiazolinone compounds, pH adjusters such as K_2PO_4 , thickeners such as xanthane gum, silica and bentonite, inert carriers such as clay, diatomaceous earth and calcium carbonate, preservatives, bonding agents, fertilizers and other active ingredients.

A water-suspendable agricultural chemical composition as claimed in the present invention may be produced using ordinary methods, such as by mixing the aforementioned active ingredients directly with the aforementioned blending vehicles and liquid or solid carriers, and/or crushing them together.

Preferably, a water-suspendable agricultural chemical composition as claimed in the present invention can be prepared in the manner described below.

(a) Composition of concentrated crushed slurry of solid agricultural chemical ingredient

A portion of various types of surfactants and other assistants (assistants are formulations aids, e.g. inert material, ingredients) are mixed by dissolving or dispersing in water followed by addition of a solid agricultural chemical ingredient. The mixture is then

suitably wet crushed with a bead mill such as a batch-type bead mill to prepare a concentrated slurry.

(b) Composition of emulsion of liquid agricultural chemical ingredient

5

Various types of surfactants and other assistants (assistants are formulations aids, e.g. inert material, ingredients) are mixed in water. An oily phase in which an oil has been dissolved is added to the liquid agricultural chemical ingredient while forcibly stirring with a homogenizer and so forth to emulsify the oily phase in the aqueous phase. This mixture is then suitably forcibly emulsified to a desired particle diameter.

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(c) Production of the composition

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The solid agricultural chemical ingredient slurry is added to the liquid agricultural chemical ingredient emulsion (in the ratio emulsion to slurry of, for example, 9:1) followed by suitably mixing with a mixer and so forth to obtain a composition.

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An herbicidal formulation according to the water-suspendable agricultural chemical composition as claimed in the present invention is preferable for controlling rice paddy weeds when under water. This is preferably carried out by applying the required amount of the water-suspendable agricultural chemical composition as claimed in the present invention directly to the rice paddy either directly or after diluting to a suitable concentration with water, or by adding to water that flows into the rice paddy (so-called spout treatment). Moreover, a composition as claimed in the present invention can also be applied simultaneously to planting by a planting machine.

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Although a water-suspendable agricultural chemical composition as claimed in the present invention can be applied in the same manner as ordinary spraying, it can also be diluted in a larger amount of water. A water-suspendable agricultural chemical composition as claimed in the present invention can be preferably used in an applied amount of 100 to 50,000 ml/ha, and more preferably 1,000 to 10,000 ml/ha.

An herbicidal formulation according to the water-suspendable agricultural chemical composition as claimed in the present invention can be used against a large number of

agronomically important weeds. The weeds to be controlled may be both monocotyledonous and dicotyledonous weeds, such as, for example, *Alisma* spp, *Leptochloa chinensis*, *Stellaria*, *Nasturtium*, *Agrostis*, *Digitaria*, *Avena*, *Setaria*, *Sinapis*, *Lolium*, *Solanum*, *Echinochloa* and especially *Echinochloa crus-galli* or *Echinochloa oryzicola*, *Scirpus* and especially *Scirpus juncoides*, *Monochoria* and especially *Monochoria vaginalis*, *Sagittaria* and especially *Sagittaria pygmaea*, *Bromus*, *Alopecurus*, *Sorghum*, *Rottboellia*, *Cyperus* and especially *Cyperus iria*, *Abutilon*, *Sida*, *Xanthium*, *Amaranthus*, *Chenopodium*, *Ipomoea*, *Chrysanthemum*, *Galium*, *Viola* and *Veronica*.

Crops of useful plants in which the combination according to the invention can be used include especially rice. The term "crops" is to be understood as also including crops that have been rendered tolerant to herbicides or classes of herbicides (for example ALS, GS, EPSPS, PPO and HPPD inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant e.g. to imidazolinones, such as imazamox, by conventional methods of breeding is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides by genetic engineering methods include e.g. glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® and LibertyLink®.

Crops are also to be understood as being those which have been rendered resistant to harmful insects by genetic engineering methods, for example Bt maize (resistant to European corn borer), Bt cotton (resistant to cotton boll weevil) and also Bt potatoes (resistant to Colorado beetle). Examples of Bt maize are the Bt-176 maize hybrids of NK® (Syngenta Seeds). The Bt toxin is a protein that is formed naturally by *Bacillus thuringiensis* soil bacteria. Examples of toxins and transgenic plants able to synthesise such toxins are described in EP-A-451 878, EP-A-374 753, WO 93/07278, WO 95/34656, WO 03/052073 and EP-A-427 529. Examples of transgenic plants that contain one or more genes which code for an insecticidal resistance and express one or more toxins are KnockOut® (maize), Yield Gard® (maize), NuCOTIN33B® (cotton), Bollgard® (cotton), NewLeaf® (potatoes), NatureGard® and Protexcta®. Plant crops and their seed material can be resistant to herbicides and at the same time also to insect feeding ("stacked" transgenic events). Seed can, for example, have the ability to express an insecticidally active Cry3 protein and at the same time be glyphosate-tolerant. The term "crops" is to be understood as also including

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crops obtained as a result of conventional methods of breeding or genetic engineering which contain so-called output traits (e.g. improved flavour, storage stability, nutritional content).

5 The following provides a more detailed explanation of the present invention through its examples. Furthermore, the present invention is not limited by these examples.

Examples:

Preliminary phytotoxicity test

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The objectives of the following phytotoxicity tests are to detect the main factors relating contact phytotoxicity caused on transplanted rice on one hand, and to check the effect of candidate materials on crop safety for the formulations according to the invention.

15 Table 1: Factors affecting phytotoxicity caused by direct contact of splashed droplet

The objective of the following tests is to identify the factors affecting the phytotoxicity caused by direct contact of splashed droplet on transplanted rice.

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Crops of rice (cv. Koshihikari) are used for the test and are placed in plastic pots (100cm plastic pot / clay loam soil). The crop condition at application is about 4.5 leaf stage. 2.5micro L/leaf are applied (on the 4th leaf) by using micro pipettes. The test is replicated two times.

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Sample No.	Description	Active Ingredient	Type of phytotoxicity		
			2DAA	4DAA	7DAA
1	Acetone	-	no phytotoxicity	no phytotoxicity	no phytotoxicity
2	Pretilachlor	Pretilachlor (131.3g/liter)	browning	browning & severe burning	severe browning & severe burning
3	Pyriftalid / bensulfuron-methyl premix	Pyriftalid (32.0g/liter) & bensulfuron-methyl (16.2g/liter)	no phytotoxicity	no phytotoxicity	no phytotoxicity
4	Pretilachlor / pyriftalid / bensulfuron-methyl (Soybean Oil)	Pretilachlor (131.3g/liter) & pyriftalid (32.0g/liter) & bensulfuron-methyl (16.2g/liter)	browning & severe burning	browning & severe burning	browning & severe burning
5	Blank	-	slight browning	slight browning	browning
6	Blank (liquid paraffin)	-	no phytotoxicity	no phytotoxicity	no phytotoxicity
7	Blank (Soybean Oil)	-	slight browning	slight browning	slight browning
8	liquid paraffin	-	no phytotoxicity	no phytotoxicity	no phytotoxicity
9	Pretilachlor + liquid paraffin	Pretilachlor (131.3g/liter)	severe browning & severe burning	severe browning & severe burning	severe browning & severe burning
10	Soybean Oil	-	no phytotoxicity	no phytotoxicity	no phytotoxicity
11	Pretilachlor + Soybean Oil	Pretilachlor (131.3g/liter)	browning	severe browning	severe browning
12	POE-POP block copolymer	-	no phytotoxicity	no phytotoxicity	no phytotoxicity
13	Pretilachlor + POE-POP block copolymer	Pretilachlor (131.3g/liter)	slight burning	severe browning & severe burning	severe browning & severe burning
14	Propylene Glycol	-	no phytotoxicity	no phytotoxicity	no phytotoxicity
15	Pretilachlor + Propylene Glycol	Pretilachlor (131.3g/liter)	severe burning	severe browning & severe burning	severe browning & severe burning

DAA means days after application.

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At the tested concentrations, pretilachlor itself is one of the most important factors in the observed contact phytotoxicity, liquid paraffin and propylene glycol are highly phytotoxic when applied together with pretilachlor, and soybean oil is better than liquid paraffin for oil phase regarding the phytotoxicity.

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Table 2: Factor affecting phytotoxicity caused by direct contact of splashed droplet

The objective of the test is to verify the effect of soybean oil and / or glycerol present in the formulations according to the invention on crop safety on transplanted rice.

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Crops of rice (cv. Koshihikari) are used for the test and are placed in plastic pots (100cm plastic pot / clay loam soil). The crop condition at application is about 4.5 leaf stage. 2.5micro L/leaf are applied (on the 4th leaf) by using micro pipettes. The test is replicated two times.

10

	w/w (%)							Type of phytotoxicity		
	Pretila- chor	Paraf- fine	Soy- bean oil	Propy- lene glycol	Glyce- rol	Aceto- ne	Water			
								2DAA	4DAA	8DAA
1	12.34 %	3.06%		5.13%		79.47 %		browning & severe burning	severe browning & severe burning	severe browning & severe burning
2	12.45 %			5.08%		82.47 %		severe burning	browning & severe burning	browning & severe burning
3	12.39 %	3.00%				84.62 %		burning	severe browning & severe burning	severe browning & severe burning
4	12.45 %		2.99%			84.56 %		slight browning	severe browning & severe burning	severe browning & severe burning
5	12.35 %		2.99%	4.98%		79.68 %		severe burning	severe browning & severe burning	severe browning & severe burning
6	12.50 %		3.00%		5.00%	79.50 %		slight wilting	burning	browning & burning
7	12.45 %		2.96%		9.98%	49.41 %	25.20 %	slight burning	severe burning	browning & burning
8	12.59 %		3.00%		15.08 %	49.85 %	19.48 %	slight burning	browning & burning	browning & burning

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	w/w (%)							Type of phytotoxicity		
	Pretila- chor	Paraf- fine	Soy- bean oil	Propy- lene glycol	Glyce- rol	Aceto- ne	Water			
								2DAA	4DAA	8DAA
9	12.23 %		2.84%		19.67 %	49.22 %	16.05 %	slight burning	burning	browning & burning
10	12.16 %		2.92%		24.90 %	38.91 %	21.11 %	slight wilting	burning	browning & burning

DAA means days after application.

- At the tested concentrations, the combination of soybean oil and glycerol is far safer than the combination of liquid paraffin and propylene glycol. Therefore, Glycerol is essential to suppress the initial phytotoxic symptom. Furthermore, the phytotoxicity is slightly reduced when glycerol content is increased.

Water-suspendable agricultural chemical compositions

- 10 Table 3: Preparation of water-suspendable agricultural chemical compositions according to the invention

	Ingredients	Formulation 1	Formulation 2	Formulation 3
Oil phase	Pretilachlor tech.	12,50% (131.3g/liter)	12,50% (132.5g/liter)	12,50% (131.3g/liter)
	Liquid paraffin	3,00%	-	
	Soybean oil		3,01%	3,01%
Solid phase	Pyriftalid tech.	3,05% (32.0g/liter)	3,07% (32.5g/liter)	3,07% (32.2g/liter)
	Bensulfuron-methyl tech.	1,54% (16.2g/liter)	1,58% (16.7g/liter)	1,58% (16.6g/liter)
Antifreeze agent	Propylene glycol	5,00%	-	-
	Glycerol	-	14,95%	5,00%
Surfactant	Tristyrylphenol ethoxylate HLB = 12.5.	0,01%	0,01%	0,01%
	POE-POP block copolymer	1,01%	1,01%	1,01%

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	Ingredients	Formulation 1	Formulation 2	Formulation 3
Biocide	1,3-benzisothiazolin-3-one	0,20%	0,20%	0,20%
pH regulator	KH ₂ PO ₄	0,50%	0,50%	0,50%
Thickener	xanthane gum	0,15%	0,15%	0,15%
Antifoam agent	Silicone-based antifoam agent	0,01%	0,01%	0,01%
Water phase	Deionized water	73,03%	63,02%	72,97%

(a) Composition of concentrated crushed slurry of solid agricultural chemical ingredient

0.1 parts by weight of Sopropore BSU (surfactant, Rhodia), 2.0 parts by weight of Epan U108 (surfactant, Daiichi Kogyo Seiyaku) and 0.1 parts by weight of Rhodosil 454 (antifoaming agent, Rhodia, silicone) and 0.1 parts by weight of Rhodopore 23 (thickener, Rhodia, xanthane gum) are mixed by dissolving or dispersing in water followed by addition of solid agricultural chemical ingredient. Either bensulfuron-methyl (common name) alone or a combination of bensulfuron-methyl and pyriftalid (common name) are used for the solid agricultural chemical ingredient. The concentration of each active ingredient in the slurry is adjusted to 15% for bensulfuron-methyl (176g/liter) and 30% for pyriftalid (352g/liter). A concentrated slurry is prepared by wet crushing with a batch-type bead mill (Imex, four-barrel sand mill, 1/8 gallon, using 1 mm glass beads) at 1000 rpm/hr (10-fold concentration of composition).

(b) Composition of emulsion of liquid agricultural chemical ingredient

An emulsifier (Epan U108, Epan U103, Epan U105 or NK-PTC), propylene glycol (antifreeze, Showa Denko), KH₂PO₄ (pH adjuster, Nippon Kayaku), xanthane gum (thickener, Rhodia) and Proxel GXL (1,3-benzisothiazolin-3-one, anti-mold agent, Arch Chemicals) are mixed in water. Refer to Tables 1 and 2 for the amounts of each ingredient added. An oily phase in which oil is dissolved is added to the liquid agricultural chemical ingredient while forcibly stirring with a homogenizer to emulsify the oily phase in the aqueous phase. Pretilachlor (common name) is used for the liquid agricultural chemical ingredient. In addition, soybean oil (Honen Corporation) or liquid paraffin (Matsuken, Moresco White P-70) is used for the oil. Refer to Tables 1 for the amounts of each ingredient added. The emulsion is forcibly emulsified for about 2 minutes to obtain the desired particle diameter.

(c) Production of water-suspendable agricultural chemical composition

The solid agricultural chemical ingredient slurry is added to the liquid agricultural chemical ingredient emulsion (ratio of emulsion to slurry = 9:1) followed by mixing for 5 minutes with a laboratory mixer having a propeller-type stirring blade attached to the shaft to obtain a composition.

Stability Test

A storage stability test is on each water-suspendable agricultural chemical composition prepared in the manner described above to follow the decomposition of the agricultural chemical ingredients in the composition, i.e. pyrifthalid, pretilachlor and bensulfuron-methyl.

100 ml of the agricultural chemical compositions prepared according to the composition method described above are sealed in glass containers and allowed to stand undisturbed in a constant temperature bath at 54°C. The agricultural chemical compositions are removed from the bath after 2 weeks followed by measurement of the content of agricultural chemical ingredients by high-performance liquid chromatography. The results are shown in Table 4.

Table 4: Storage stability test performed on the agricultural chemical compositions according to the invention

Remaining active ingredient after 2 weeks at 54°C	Formulation 1	Formulation 2	Formulation 3
Pyrifthalid (%)	99,70%	100%	100%
Pretilachlor (%)	99,30%	99,90%	100%
Bensulfuron-methyl (%)	81,90%	82,90%	83,50%

The water-suspendable agricultural chemical composition according to the present invention, that contains a liquid agricultural chemical ingredient and a solid agricultural chemical ingredient, ensures satisfactory suspension or dispersion of the contained

ingredients and prevents their decomposition while also inhibiting their precipitation and aggregation even when stored for a long period of time. The storage stability of the improved formulations comprising soybean oil and glycerol (formulations 2 & 3) is very similar to the storage stability of the formulation comprising liquid paraffin and propylene glycol.

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Table 5: Phytotoxicity tests carried out with the improved formulation according to the invention

	Formula 1	Formula 2	Formula 3
Bensulfuron-methyl tech.	1.58% (16.6g/liter)	1.58% (16.7g/liter)	1.56% (16.4g/liter)
Pyrifthalid tech.	3.07% (32.2g/liter)	3.07% (32.5g/liter)	3.09% (32.4g/liter)
Pretilachlor tech.	12.50% (131.3g/liter)	12.50% (132.5g/liter)	12.56% (131.9g/liter)
Soybean Oil	3.01%	3.01%	3.01%
Tristyrylphenol ethoxylate HLB = 12.5.	0.01%	0.01%	0.01%
POE-POP block copolymer	1.01%	1.01%	1.00%
1,3-benzisothia-zolin-3- one	0.20%	0.20%	0.20%
Propylene glycol	-	-	0.51%
Glycerol	5.00%	14.95%	4.48%
KH ₂ PO ₄	0.50%	0.50%	0.50%
Xanthane gum	0.15%	0.15%	0.15%
Silicone-based antifoam agent	0.01%	0.01%	0.01%
Deionized water	72.97%	63.02%	72.93%
Level of phytotoxicity*: 1DAA	1*	0*	1*
Level of phytotoxicity*: 2DAA	1*	0*	1*
Level of phytotoxicity*: 3DAA	2*	1*	2*
Level of phytotoxicity*: 7DAA	2*	1*	2*

* 0 = no damage,

* 1 = no practical damage but some symptom,

* 2 = marginal damage, and

* 3 = unacceptable damage.

DAA means days after application.

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At the tested concentrations, the improved formulations 2 and 3 according to the instant invention comprising glycerol and soybean oil are far safer than the formulations comprising propylene glycol and liquid paraffin (formulation 1), and formulation 2 which
5 comprises 14,95% of glycerol is safer than formulation 3 which comprises only 4,48% of glycerol.

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What is claimed is:

1. A water-suspendable agricultural chemical composition comprising at least one liquid agricultural chemical ingredient, at least one solid agricultural chemical ingredient, at least
5 one oil and at least one poly-ol comprising at least 3 hydroxyl groups.
2. The composition according to claim 1 wherein the oil is selected from the group consisting of mineral oil, vegetable oil, fatty acid ester, epoxidized vegetable oil and liquid paraffin.
- 10 3. The composition according to either claims 1 or 2 wherein the oil is a vegetable oil.
4. The composition according to any one of claims 1 or 3 wherein the vegetable oil is soybean oil.
- 15 5. The composition according to any one of claims 1 to 4 wherein the poly-ol is glycerol.
6. The composition according to any one of claims 1 to 5 comprising at least one nonionic surfactant.
- 20 7. The composition according to any one of claims 1 to 6 wherein the nonionic surfactant is polyoxyethylene-polyoxypropylene block polymer.
8. The composition according to any one of claims 1 to 7 wherein the liquid or solid agricultural chemical ingredient is at least one herbicide.
- 25 9. The composition according to any one of claims 1 to 8 wherein the liquid or solid agricultural chemical ingredient is at least one insecticide.
10. The composition according to any one of claims 1 to 9 wherein the liquid or solid
30 agricultural chemical ingredient is at least one bactericide.
11. The composition according to any one of claims 1 to 7 comprising at least one bactericide and at least one insecticide as agricultural chemical ingredients.

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12. The composition according to any one of claims 1 to 8 wherein at least one of the liquid agricultural chemical ingredients is a chloroacetamide-based herbicide.

5 13. The composition according to claim 12 wherein the chloroacetamide-based herbicide is pretilachlor.

14. The composition according to any one of claims 1 to 8 and 12 to 13 wherein at least one of the solid agricultural chemical ingredients is a sulfonylurea-based herbicide.

10 15. The composition according to claim 14 wherein the sulfonylurea-based herbicide is bensulfuron-methyl.

16. The composition according to any one of claims 1 to 8 and 12 to 15 that further comprises pyriftalid as a solid agricultural chemical ingredient.

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17. A method of controlling undesired vegetation in crops of useful plants, which comprises allowing an effective amount of the composition as defined in any one of claims 1 to 16 to act where control is desired.

20 18. The method according to claim 17, wherein the crop of useful plants is rice.

19. Use of the composition as defined in any one of claims 1 to 16 for controlling grasses and weeds in crops of useful plants.

25 20. The use according to claim 19 wherein the crop of useful plants is rice.

21. A method for the preparation of the composition as defined in any one of claims 1 to 16, by blending an oil into a water-suspendable agricultural chemical composition comprising at least one liquid agricultural chemical ingredient and at least one solid agricultural chemical
30 ingredient.

22. Use of at least one poly-ol comprising at least 3 hydroxyl groups in compositions as defined in any one of claims 1 to 16 to reduce the contact injury of pretilachlor on leaves of crops of useful plants.

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23. The use according to claim 22 wherein the poly-ol is glycerol.

24. The use of at least one poly-ol according to either claims 22 or 23 in admixture with soybean oil in compositions as defined in any one of claims 1 to 16 to reduce the contact
5 injury of pretilachlor on leaves of crops of useful plants.

25. The use according to any one of claims 22 to 24 wherein the crop of useful plants is rice.