



(51) International Patent Classification:

A01N 47/38 (2006.01) A01N 25/02 (2006.01)
A01P 13/02 (2006.01)

(21) International Application Number:

PCT/EP2024/058100

(22) International Filing Date:

26 March 2024 (26.03.2024)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

23165970.7 31 March 2023 (31.03.2023) EP

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ,
CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG,
KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY,
MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA,
NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO,
RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH,
TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS,
ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, CV,
GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST,
SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ,
RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ,
DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT,
LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE,
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN,
GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))

Published:

— with international search report (Art. 21(3))
— in black and white; the international application as filed
contained color or greyscale and is available for download
from PATENTSCOPE

(54) Title: EMULSIFIABLE CONCENTRATE (EC) FORMULATION WITH THIENCARBAZONE-METHYL

(57) Abstract: The present invention relates to emulsifiable concentrate formulations comprising thien carbazole-methyl or an agro-chemically acceptable salt thereof, one or more organic water-immiscible solvents, one or more organic water-miscible solvents selected from linear and cyclic carbonate esters, one or more emulsifier, and one or more organic bases, wherein the formulation exhibits a pH of between pH 5.5 and pH 9.

Emulsifiable Concentrate (EC) formulation with thiencarbazone-methyl**Technical field**

The present invention relates to the field of crop protection compositions. In particular, the invention relates to emulsifiable concentrate (EC) formulations comprising herbicidally active compounds from the group of the sulfonylaminocarbonyltriazolinones.

Background

In general, active compounds for crop protection are not employed in pure form. Depending on the area of use and the type of use, and on physical, chemical and biological parameters, the active compound is used as an active compound formulation in a mixture with customary auxiliaries and additives. Also known are combinations with further active compounds for widening the activity spectrum and/or for protecting crop plants (for example by safeners, antidotes).

Formulations of individual active compounds, like formulations of combinations of a plurality of active compounds for crop protection, should generally be easy to apply and easy to use and have broad biological action combined with high selectivity with respect to the active compounds used, and should additionally be easy to formulate in the preparation process. Of particular importance here is high chemical and physical stability (storage stability) of the formulation.

Typical formulations in crop protection are concentrated suspensions (active compound suspensions) in which the active compound particles (discontinuous phase) are suspended in an external liquid phase (continuous phase). Depending on the nature of the external phase, the suspensions are classified as suspension concentrates (SC), where the main component of the external phase is water, or oil dispersions (OD), where the main component of the external phase is an organic solvent. The choice of the respective external phase is frequently determined by the stability of the active compounds in question. In general, active compounds which are unstable in water are formulated as OD, and active compounds which are unstable in organic solvents are formulated as SC.

Sulfonylaminocarbonyltriazolinones are a class of highly effective and selective herbicides, that are described in WO 01/05788, WO 03/026426 and WO 03/026427. Thiencarbazone methyl (methyl 4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl)carbonylsulfamoyl]-5-methylthiophene-3-carboxylate; CAS 317815-83-1) also belongs to said class of sulfonylaminocarbonyltriazolinones. These herbicides are typically formulated as oil dispersions, as described in WO 2005/051082. Suspension concentrates of sulfonylaminocarbonyltriazolinones are also known, e.g. EP2170041.

While OD and SC formulations of sulfonylaminocarbonyltriazolinones have been shown to provide for an adequate storage stability and broad biological action, these formulations are generally difficult to prepare and handle.

Therefore, it was an object of the present invention to provide an improved formulation of crop protection agents, in particular of sulfonylaminocarbonyltriazolinones, which has a high chemical and physical stability, and is easy to handle in terms of production as well as field application.

Summary

This object is achieved by the specific emulsifiable concentrate (EC) formulation of the present invention.

Accordingly, the present invention relates to an emulsifiable concentrate (EC) formulation comprising

- 10 a) one or more herbicidally active compounds from the group of the sulfonylaminocarbonyltriazolinones, preferably thienecarbazone-methyl or an agrochemically acceptable salt thereof,
- b) one or more organic water-immiscible solvents,
- c) one or more organic water-miscible solvents,
- 15 d) one or more emulsifiers,
- e) one or more organic bases,

wherein the formulation exhibits a pH of between pH 5.5 and pH 9.

The pH of the formulation may be measured after diluting the emulsifiable concentrate formulation in distilled water to obtain a 10 % w/w mixture.

- 20 The pH of the formulation may be in particular be measured by the following method:
- diluting the emulsifiable concentrate formulation in distilled water to obtain a 10 % w/w mixture;
 - stirring the mixture with a magnetic stirrer at 1500 RPM for 10 minutes at 25°C; and
 - measuring the pH of the stirred mixture at 25 °C with a pH meter until the measured pH is stable for 10s.

- 25 The pH measurement may be performed with a Knick 766 pH meter (Calimatic, Knick SE 100N).

The EC formulation may further comprise one or more of the following:

- f) one or more safeners,
- g) one or more agrochemically active ingredients different from a) and f),

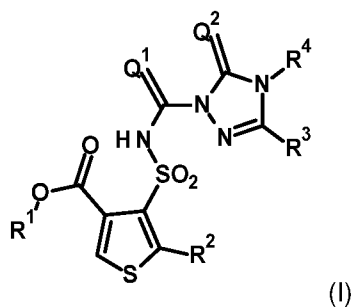
- h) further adjuvants compatible with agrochemical formulations, wetting agents and/or other additives.

The term “emulsifiable concentrate” (abbreviated with “EC”) is known in the art. Emulsifiable concentrate (EC) formulations conventionally contain an active ingredient, one or more surfactants which act as emulsifiers upon dilution of the EC with water, and a water immiscible solvent.

The term “water miscible” means the compound or solvent may have a solubility in water at 20 °C of at least 5 g/l, preferably of at least 20 g/l, more preferably at least 50 g/l, and in particular of at least 100 g/l.

The term “water immiscible” means the compound or solvent may have a solubility in water at 20 °C of up to 100 g/l, preferably of up to 50 g/l °C, more preferably up to 20 g/l, and in particular of up to 5 g/l.

- 10 Sulfonylaminocarbonyltriazolinones are described in WO 01/05788. Sulfonylaminocarbonyltriazolinones are of the general formula (I)



in which

Q¹ represents O (oxygen) or S (sulphur),

- 15 Q² represents O (oxygen) or S (sulphur),

R¹ represents in each case optionally substituted alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, heterocyclyl or heterocyclalkyl,

R² represents hydrogen, cyano, nitro, halogen or represents in each case optionally substituted alkyl, alkoxy, alkoxycarbonyl, alkylthio, alkylsulphinyl, alkylsulphonyl, alkenyl, alkynyl, alkenyloxy or alkyloxy,

R³ represents hydrogen, hydroxyl, mercapto, amino, cyano, halogen or represents in each case optionally substituted alkyl, alkenyl, alkynyl, alkoxy, alkylthio, alkylamino, alkylcarbonylamino, alkenyloxy, alkyloxy, alkenylthio, alkylthio, alkenylamino, alkylamino, dialkylamino, aziridino, pyrrolidino, piperidino, morpholino, cyclo alkyl, cycloalkenyl, cycloalkyloxy, cycloalkylthio, cycloalkylamino,

cycloalkylalkyl, cycloalkylalkoxy, cycloalkylalkylthio, cycloalkyl-alkylamino, aryl, arylalkyl, aryloxy, arylalkoxy, arylthio, arylalkylthio, arylamino or arylalkylamino, and

R⁴ represents hydrogen, hydroxyl, amino, cyano, represents alkylideneamino or represents in each case optionally substituted alkyl, alkenyl, alkynyl, alkoxy, alkylamino, alkyl-carbonylamino, alkenyloxy, 5 dialkylamino, cycloalkyl, cycloalkylamino, cycloalkylalkyl, aryl or arylalkyl, or

R³ and R⁴ together represent optionally branched alkanediyl,

and salts of the compounds of the formula (I).

Thienecarbazone-methyl (Methyl 4-[(4,5-dihydro-3-methoxy-4-methyl-5-oxo-1H-1,2,4-triazol-1-yl)carbonylsulfamoyl]-5-methylthiophene-3-carboxylate; CAS No.317815-83-1) is also described in 10 WO 01/05788. Thienecarbazone-methyl can be provided in form of its salt, preferably in form of its sodium salt.

Preferably, the EC formulation exhibits a pH of between 6.0 and 8.5, further preferably between 6.5 and 8.0, even further preferably between 6.8 and 7.7. The pH may be measured as described above.

The pH of the EC is preferably adjusted by the at least one or more organic base.

15 It has been found that EC formulations comprising sulfonylaminocarbonyltriazolinones, preferably thienecarbazone-methyl, require a certain pH to be chemically stable. When the pH is too acidic or too basic, the sulfonylaminocarbonyltriazolinone will degrade to a significant percentage. By use of an organic base, the pH may be adjusted properly to allow for a storage-stable EC formulation.

In a further embodiment, the emulsifiable concentrates according to the invention may comprise

- 20 a) 0.01 to 5 % by weight, preferably from 0.1 to 2 % by weight, further preferably 0.3 to 1 % by weight of one or more herbicidally active compounds from the group of the sulfonylaminocarbonyltriazolinones, preferably thienecarbazone-methyl or an agrochemically acceptable salt thereof; and/or
- b) 5 to 95 % by weight, preferably 10 to 70 % by weight, further preferably 20 to 60 % by weight 25 of the one or more organic water-immiscible solvents; and/or
- c) 5 to 95 % by weight, preferably 10 to 60 % by weight, further preferably 20 to 40 % by weight of the one or more organic water-miscible solvents; and/or
- d) 0.1 to 30 % by weight, preferably 1 to 25 % by weight, further preferably 5 to 20 % by weight of the one or more emulsifiers; and/or
- 30 e) 0.1 to 10 % by weight, preferably 0.2 to 5 % by weight, further preferably 0.5 to 2 % by weight of the organic base.

The EC formulation may further comprise one or more of the following:

- f) 0 to 10 % by weight, preferably 1 to 8 % by weight, further preferably 2 to 6 % by weight of one or more safeners; and/or
- g) 0 to 40 % by weight, preferably 5 to 30 % by weight, further preferably 10 to 25 % by weight of one or more agrochemically active ingredients different from a) and f); and/or
- h) 0 to 40 % by weight, preferably 5 to 30 % by weight, further preferably 10 to 20 % by weight of further adjuvants compatible with agrochemical formulations, wetting agents and/or other additives.

Here and in the entire description, the term "% by weight" refers to the relative weight of the component in question based on the total weight of the formulation, unless defined otherwise.

The organic water-immiscible solvent b) may be a hydrocarbon, which may be unsubstituted or substituted.

Examples for the organic water-immiscible solvent b) are aromatic hydrocarbons, for example mono- or polyalkyl-substituted benzenes, such as toluene, xylenes, mesitylene, ethylbenzene, or mono- or polyalkyl-substituted naphthalenes, such as 1-methylnaphthalene, 2-methylnaphthalene or dimethylnaphthalene, or other benzene-derived aromatic hydrocarbons, such as indane or Tetralin®, or mixtures thereof; aliphatic hydrocarbons, for example straight-chain or branched aliphatics, for example of the formula C_nH_{2n+2} , such as pentane, hexane, octane, 2-methylbutane or 2,2,4-trimethylpentane, or cyclic, optionally alkyl-substituted aliphatics, such as cyclohexane or methylcyclopentane, or mixtures thereof, such as solvents of the Exxsol® D series, Isopar® series or Bayol® series, for example Bayol® 82 (ExxonMobil Chemicals), or the Isane® IP series or Hydroseal®G series (TotalFinaElf); mixtures of aromatic and aliphatic hydrocarbons, such as solvents of the Solvesso® series, for example Solvesso®100, Solvesso®150 or Solvesso® 200 (ExxonMobil Chemicals), of the Solvarex®/Solvaro® series (TotalFinaElf) or the Caromax® series, for example Caromax® 28 (Petrochem Carless); or halogenated hydrocarbons, such as halogenated aromatic and aliphatic hydrocarbons, such as chlorobenzene or methylene chloride.

Alternatively, the organic water-immiscible solvent b) can be selected from fatty acid esters, for example of natural origin, for example natural oils, such as animal oils or vegetable oils, or of synthetic origin, for example the Edenor® series, for example Edenor® MEPa or Edenor® MESU, or the Agnique® ME series or Agnique® AE series (Cognis), the Salim® ME series (Salim), the Radia® series, for example Radia® 30167 (ICI), the Prilube® series, for example Prilube® 1530 (Petrofina), the Stepan® C series (Stepan) or the Witconol®23 series (Witco). The fatty acid esters are preferably esters of C_{10} - C_{22} -, with preference C_{12} - C_{20} -, fatty acids. The C_{10} - C_{22} -fatty acid esters are, for example, esters of unsaturated or saturated C_{10} - C_{22} -fatty acids, in particular those having an even number of carbon atoms, for example erucic acid, lauric

acid, palmitic acid, and in particular C₁₈-fatty acids, such as stearic acid, oleic acid, linoleic acid or linolenic acid. Examples of fatty acid esters such as C₁₀-C₂₂-fatty acid esters are glycerol and glycol esters of fatty acids such as C₁₀-C₂₂-fatty acids, or transesterification products thereof, for example fatty acid alkyl esters such as C₁₀-C₂₂-fatty acid C₁-C₂₀-alkyl esters, which can be obtained, for example, by transesterification of the abovementioned glycerol or glycol fatty acid esters such as C₁₀-C₂₂-fatty acid esters with C₁-C₂₀-alcohols (for example methanol, ethanol, propanol or butanol). The transesterification can be carried out by known methods, as described, for example, in Roempp Chemie Lexikon, 9th edition, volume 2, page 1343, Thieme Verlag Stuttgart. Preferred fatty acid alkyl esters such as C₁₀-C₂₂-fatty acid C₁-C₂₀-alkyl esters are methyl esters, ethyl esters, propyl esters, butyl esters, 2-ethylhexyl esters and dodecyl esters. Preferred glycol and glycerol fatty esters such as C₁₀-C₂₂-fatty acid esters are the uniform or mixed glycol esters and glycerol esters of C₁₀-C₂₂-fatty acids, in particular of such fatty acids having an even number of carbon atoms, for example erucic acid, lauric acid, palmitic acid and in particular C₁₈-fatty acids such as stearic acid, oleic acid, linoleic acid or linolenic acid.

Animal oils are generally known and commercially available. For the purpose of the present invention, the term "animal oils" is to be understood as meaning, for example, oils of animal origin such as whale oil, cod-liver oil, musk oil or mink oil.

Vegetable oils are generally known and commercially available. For the purpose of the present invention, the term "vegetable oils" is to be understood as meaning, for example, oils of oleaginous plant species, such as soybean oil, rapeseed oil, corn oil, sunflower oil, cottonseed oil, linseed oil, coconut oil, palm oil, thistle oil, walnut oil, arachis oil, olive oil or castor oil, in particular rapeseed oil, where the vegetable oils also include their transesterification products, for example alkyl esters, such as rapeseed oil methyl ester or rapeseed oil ethyl ester.

The vegetable oils are preferably esters of C₁₀-C₂₂-, preferably C₁₂-C₂₀-, fatty acids. The C₁₀-C₂₂-fatty acid esters are, for example, esters of unsaturated or saturated C₁₀-C₂₂-fatty acids having, in particular, an even number of carbon atoms, for example erucic acid, lauric acid, palmitic acid and in particular, C₁₈-fatty acids such as stearic acid, oleic acid, linoleic acid or linolenic acid.

Examples of vegetable oils are C₁₀-C₂₂-fatty acid esters of glycerol or glycol with C₁₀-C₂₂-fatty acids, or C₁₀-C₂₂-fatty acid C₁-C₂₀-alkyl esters which can be obtained, for example, by transesterification of the glycerol or glycol C₁₀-C₂₂-fatty acid esters mentioned above with C₁-C₂₀-alcohols (for example methanol, ethanol, propanol or butanol). The transesterification can be carried out by known methods as described, for example, in Roempp Chemie Lexikon, 9th edition, volume 2, page 1343, Thieme Verlag Stuttgart.

The vegetable oils can be contained in the adjuvants according to the invention for example in the form of commercially available vegetable oils, in particular rapeseed oils, such as rapeseed oil methyl ester, for example Phytorob® B (Novance, France), Edenor® MESU and the Agnique® ME series (Cognis,

Germany), the Radia® series (ICI), the Prilube® series (Petrofina), or biodiesel or in the form of commercially available, plant-oil-containing formulation additives, in particular those based on rapeseed oils, such as rapeseed oil methyl esters, for example Hasten® (Victorian Chemical Company, Australia, hereinbelow referred to as Hasten, main ingredient: rapeseed oil ethyl ester), Actirob® B (Novance, France, hereinbelow referred to as ActirobB, main ingredient: rapeseed oil methyl ester), Rako-Binol® (Bayer AG, Germany, hereinbelow referred to as Rako-Binol, main ingredient: rapeseed oil), Renol® (Stefes, Germany, hereinbelow referred to as Renol, vegetable oil ingredient: rapeseed oil methyl ester) or Stefes Mero® (Stefes, Germany, hereinbelow referred to as Mero, main ingredient: rapeseed oil methyl ester).

- 10 Examples of synthetic fatty acid esters are, for example, those derived from fatty acids having an odd number of carbon atoms, such as C₁₁-C₂₁-fatty acid esters.

Preferred organic water-immiscible solvents b) are aromatic hydrocarbons and/or aliphatic hydrocarbons.

The organic water- immiscible solvent b) can be present on its own or in a mixture of different water-immiscible solvents.

- 15 The organic water- miscible solvent c) is preferably a linear or cyclic alkyl carbonate, in particular methyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate and isomers thereof, propylene carbonate, glycerol-1,2-carbonate and butylene carbonate, or a mixture thereof.

Further preferably, the organic water-miscible solvent c) is propylene carbonate and/or glycerol-1,2-carbonate, even further preferably propylene carbonate.

- 20 Surprisingly, it has been found that sulfonylaminocarbonyltriazolinones, preferably thienecarbazone-methyl, are chemically significantly stabilized in a biphasic solvent system comprising a water-immiscible solvent and a water-miscible solvent, wherein the latter is a linear or cyclic carbonate. Such carbonates, in combination with a suitable pH between 5.5 and 9, preferably 6 and 8.5, further preferably 6.5 and 8.0, even further preferably between 6.8 and 7.7, effectively prevent chemical degradation of the a.i. over time.

- 25 The EC formulation according to the invention comprises as an additional essential component d) also at least one suitable emulsifier component enabling an oil-in-water emulsion to be formed when the EC formulation of the invention is added to water.

The emulsifier can be an ionic (cationic or anionic), amphoteric or non-ionic surfactant, such as ionic or non-ionic or amphoteric emulsifier or a mixture thereof, including standard surface-active substances

- 30 present in formulations of active agrochemical ingredients.

The emulsifier may be at least one non-ionic surfactant selected from the group of alkoxyated alcohols, ethoxyated alcohols, ethopropoxyated alcohols, alkylphenoethoxyates, alkoxyated tristyrylphenols, alkoxyated tributylphenols, alkylaminethoxyates, ethoxyated vegetable oils including their hydrogenates, polyadducts of ethylene oxide and propylene oxide (e.g. polyoxyethylene-polyoxypropylene block copolymers and their derivatives), ethoxyated fatty acids, nonionic polymeric surfactants (e.g. polyvinylalcohol, polyvinylpyrrolidone, polymethacrylates and their derivatives), sorbitan esters and their ethoxyates, sorbitolesters, propylene glycol esters of fatty acids and polyglycerolesters.

Examples of preferred non-ionic surfactants are ethoxyated alcohols (e.g. Brij 020-SO-(MV), Croda), ethopropoxyated alcohols (e.g. Agnique KE 3551, BASF), alkoxyated tristyrylphenols, ethoxyated tristyrylphenols (e.g. Soprophor TS/16, Rhodia), ethopropoxyated tristyrylphenols (e.g. Soprophor 796/P, Rhodia) and ethoxyated vegetable oils (e.g. Tanemul® KS, Tanatex Chemicals).

Examples of suitable anionic surfactants include, but are not limited to, salts of polyacrylic acid, salts of polymers of mixtures of acrylic acid/acrylate esters, salts of polymers of mixtures of acrylic acid/styrene, salts of lignosulfonic acid (such as sodium lignosulfonate), salts of phenolsulfonic acid, salts of condensation products of phenolsulphonic acid and formaldehyde, salts of naphthalenesulfonic acid, salts of naphthalenesulphonic acid and formaldehyde condensation products, salts of sulfonates of condensed naphthalenes or alkyl naphthalenes, salts of sulfonates of dodecyl- and tridecylbenzenes, salts of sulfosuccinic or sulfosuccinamate esters, salts of alkyl sulfates, salts of alkyl polyethoxyated and/or polypropoxyated sulfates, salts of paraffin sulfonates, salts of alkyl sulfonates, salts of alkyl polyethoxyated and/or polypropoxyated sulfonates, salts of aryl sulfates, salts of aryl polyethoxyated and/or polypropoxyated sulfates, salts of aryl sulfonates, salts of aryl polyethoxyated and/or polypropoxyated sulfonates, salts of alkylaryl sulfates, salts of alkylaryl polyethoxyated and/or polypropoxyated sulfates, salts of alkylaryl sulfonates, salts of alkylaryl polyethoxyated and/or polypropoxyated sulfates, salts of diphenyl sulfonates, and of diphenyloxide sulfonates, salts of alpha-olefinsulfonates, salts of sulfonates of fatty acids and oils, salts of alpha-sulfonated methyl esters, salts of taurine derivatives (preferably alkyl taurates), salts of isethionates, salts of alkyl phosphoric esters, salts of aryl phosphoric esters, salts of alkylaryl phosphoric esters, salts of phosphoric esters of polyethoxyated and/or polypropoxyated aliphatic linear or branched alcohols, salts of phosphoric esters of polyethoxyated and/or polypropoxyated aryl alcohols, protein hydrolysates, lignosulfite waste liquors, salts of polystyrenesulphonic acids, salts of polyvinylsulphonic acids, salts of carboxylates, salts of ether carboxylates.

Examples for such surfactants or emulsifiers are: Ether carboxylates, sulfonates, sulfates, and phosphates, and their inorganic salts (e.g., alkali metal, alkaline earth metal or ammonium salts) and organic salts (e.g., amine- or alkanolamine-based salts), such as Genapol®LRO, Sandopan® products,

Hostaphat/Hordaphos® products from Clariant, Servoxyl® products from Elementis, Agnique® SLS products (Cognis); salts of aliphatic, cycloaliphatic, and olefinic carboxylic acids and polycarboxylic acids, and also alpha-sulfo fatty acid esters as obtainable from Cognis, Sulfosuccinates, alkanesulfonates, paraffinsulfonates and olefinsulfonates and their inorganic (e.g., alkali metal and alkaline earth metal) and

5 organic (e.g., amine- or alkanolamine-based) salts such as Netzer IS®, Hoe®S1728, Hostapur®OS, Hostapur®SAS from Clariant, Triton®GR7ME and GR5 from Dow, Empimin® products from Huntsman, Marlon®-PS65 from Condea, Sulfosuccinamates such as the Aerosol® products from Cytec or the Empimin® products from Huntsman, Surface-active polyacrylic and polymethacrylic derivatives such as the Sokalan® products from BASF.

- 10 Preferred anionic emulsifiers are: phosphated or sulfated (poly)alkylphenol alkoxyates, phosphated or sulfated poly(arylalkyl)-phenol alkoxyates, (poly)alkyl- and poly(arylalkyl)-benzenesulfonates in acidic or salt form and sulfosuccinates.

More preferred anionic emulsifiers are emulsifiers based on calcium salt of dodecylbenzenesulfonic acid, such as Rhodacal® 60 BE (Rhodia) or Calsogen® 4814 (Clariant), Atlox® 4838B X-MSU (Croda),

- 15 Ninate® 60E X-MSU (Stepan) or Nansa® EVM 70/2E (Huntsman).

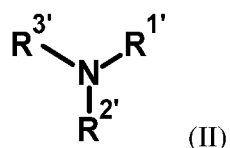
The one or more organic base e) may be selected from amine-based organic compounds, preferably selected from alkylamines, amino alcohols, alkylamino alcohols, aromatic amines, (poly)ethoxylated amines and (poly)ethoxylated/propoxylated amines.

- The organic base is used for pH adjustment of the formulation. By adjusting the pH to a range between
- 20 5.5. and 9, preferably pH 6.0 and 8.5, further preferably between pH 6.5 and 8.0, the a.i. is chemically stabilized.

The organic base, in particular the amine-based organic compound, is preferably soluble in the biphasic solvent system of the water-immiscible solvent and the water-miscible solvent, in particular in the provided concentration ranges.

- 25 The alkylamine may be, for example, triethylamine, the aromatic amine may be for example pyridine. The amino alcohol may be for example triethanolamine.

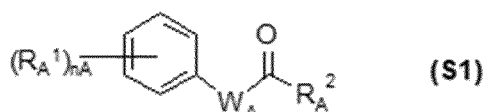
Preferably, the organic base is an (poly)ethoxylated amine, such as a fatty amine ethoxylate of the following formula (II)



with $R^{1'}$ being straight chain or branched alkyl, preferably unsubstituted, straight chain C_{2-24} alkyl, $R^{2'}$ being $-(CH_2-CH_2-O)_xH$, and $R^{3'}$ being $-(CH_2-CH_2-O)_yH$ with $x+y$ being between 2 and 20. Examples are stearylamine with 8 mol EO (e.g. Genamin S080 by Clariant) and an amine ethoxylate based on coconut fatty amine (e.g. Genamin C050 by Clariant).

- 5 In a further embodiment, the one or more organic base is selected from amine-based organic bases and the one or more organic water-miscible solvents is selected from methyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate and isomers thereof, propylene carbonate, glycerol-1,2-carbonate and butylene carbonate. Preferably, the one or more organic base is an ethoxylated amine and the one organic water- miscible solvent is propylene carbonate.
- 10 The emulsifiable concentrates according to the invention may comprise, as component f), safeners which are suitable for reducing or preventing damage to the crop plant. Suitable safeners are known, for example, from WO-A-96/14747 and the literature cited therein. In the organic solvent, the safeners are present in dissolved form.

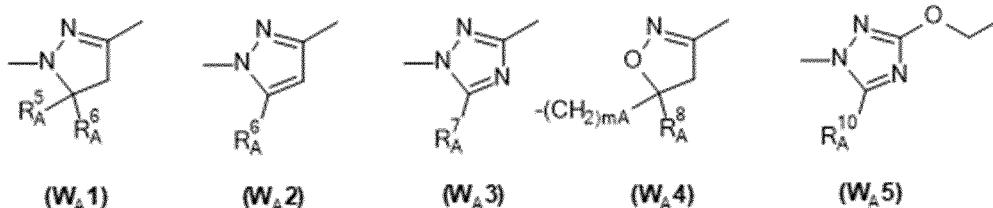
S1) Compounds from the group of heterocyclic carboxylic acid derivatives (formula S1)



15

wherein symbols and indices are defined as follows:

- n_A is an integer value in the range of 0 to 5, preferably 0 to 3;
- R_A^1 is halogen, (C_1-C_4) -alkyl, (C_1-C_4) -alkoxy, nitro or (C_1-C_4) -haloalkyl;
- 20 W_A is an unsubstituted or substituted divalent heterocyclic moiety selected from the group of partially unsaturated or aromatic five-membered heterocycles carrying 1 to 3 hetero ring atoms selected from the group of nitrogen (N) and oxygen (O), and carrying at least one N-atom and not more than one O-atom in the ring, preferably a five-membered heterocyclic moiety selected from the group (W_A^1) to (W_A^4) ,



25

m_A is 0 or 1;

R_A^2 is OR_A^3 , SR_A^3 or $NR_A^3R_A^4$ or a saturated or unsaturated 3- to 7-membered heterocycle containing at least one N-atom and up to 3 heteroatoms, preferably combined with other heteroatoms from

the group of O (oxygen) and S (sulfur), and which is linked to the carbonyl group in (S1) via a nitrogen atom, and which is unsubstituted or substituted by moieties selected from the group of (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy or possibly substituted phenyl, preferably OR_A³, NHR_A⁴ oder N(CH₃)₂, particularly OR_A³

5 R_A³ is hydrogen or an unsubstituted or substituted aliphatic hydrocarbon moiety, preferably containing 1 to 18 C-atoms;

R_A⁴ is hydrogen, (C₁-C₆)-alkyl, (C₁-C₆)-alkoxy or substituted or unsubstituted phenyl;

R_A⁵ is hydrogen, (C₁-C₈)-alkyl, (C₁-C₈)-haloalkyl, (C₁-C₄)-alkoxy-(C₁-C₈)-alkyl, cyano or COOR_A⁹,
 10 wherein R_A⁹ is hydrogen, (C₁-C₈)-alkyl, (C₁-C₈)-haloalkyl, (C₁-C₄)-alkoxy-(C₁-C₄)-alkyl, (C₁-C₆)-hydroxyalkyl, (C₃-C₁₂)-cycloalkyl oder tris-(C₁-C₄)-alkylsilyl;

R_A⁶, R_A⁷, R_A⁸ are independently hydrogen, (C₁-C₈)-alkyl, (C₁-C₈)-haloalkyl, (C₃-C₁₂)-cycloalkyl or substituted or unsubstituted phenyl;

R_A¹⁰ is hydrogen, (C₃-C₁₂)-cycloalkyl, substituted or unsubstituted phenyl, or substituted or unsubstituted heteroaryl;

15

S1^a) Compounds of the dichlorophenylpyrazoline-3-carboxylic acid type (S1^a), preferably compounds such as 1-(2,4-dichlorophenyl)-5-(ethoxycarbonyl)-5-methyl-2-pyrazoline-3-carboxylic acid, ethyl 1-(2,4-dichlorophenyl)-5-(ethoxycarbonyl)-5-methyl-2-pyrazoline-3-carboxylate (S1-1) ("mefenpyr-diethyl"), and related compounds as described in WO-A-
 20 91/07874;

S1^b) Derivatives of dichlorophenylpyrazolecarboxylic acid (S1^b), preferably compounds such as ethyl 1-(2,4-dichlorophenyl)-5-methylpyrazole-3-carboxylate (S1-2), ethyl 1-(2,4-dichlorophenyl)-5-isopropylpyrazole-3-carboxylate (S1-3), ethyl 1-(2,4-dichlorophenyl)-5-(1,1-dimethylethyl)pyrazole-3-carboxylate (S1-4) and related compounds as described in EP-A-
 25 333131 and EP-A-269806;

S1^c) Derivatives of 1,5-diphenylpyrazole-3-carboxylic acid (S1^c), preferably compounds such as ethyl 1-(2,4-dichlorophenyl)-5-phenylpyrazole-3-carboxylate (S1-5), methyl 1-(2-chlorophenyl)-5-phenylpyrazole-3-carboxylate (S1-6) and related compounds as described, for example, in EP-A-268554;

30 S1^d) Compounds of the triazolecarboxylic acid type (S1^d), preferably compounds such as fenchlorazole-(ethyl ester), i.e. ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl-1H-1,2,4-triazole-3-carboxylate (S1-7), and related compounds, as described in EP-A-174562 and EP-A-346620;

S1^e) Compounds of the 5-benzyl- or 5-phenyl-2-isoxazoline-3-carboxylic acid or of the 5,5-diphenyl-
 35 2-isoxazoline-3-carboxylic acid type (S1^e), preferably compounds such as ethyl 5-(2,4-dichlorobenzyl)-2-isoxazoline-3-carboxylate (S1-8) or ethyl 5-phenyl-2-isoxazoline-3-carboxylate (S1-9) and related compounds as described in WO-A-91/08202, or 5,5-diphenyl-2-

isoxazolinecarboxylic acid (S1-10) or ethyl 5,5-diphenyl-2-isoxazoline-3-carboxylate (S1-11) ("isoxadifen-ethyl") or n-propyl 5,5-diphenyl-2-isoxazoline-3-carboxylate (S1-12) or ethyl 5-(4-fluorophenyl)-5-phenyl-2-isoxazoline-3-carboxylate (S1-13) as described in patent application WO-A-95/07897.

- 5 S1^a) compounds of the triazolyloxy acetic acid type (S1^a), preferably compounds such as methyl-
 {[1,5-bis(4-chloro-2-fluorophenyl)-1H-1,2,4-triazol-3-yl]oxy}acetate (S1-14) or {[1,5-Bis(4-
 chloro-2-fluorophenyl)-1H-1,2,4-triazol-3-yl]oxy}acetic acid (S1-15) or methyl-5-(4-chloro-
 2-fluorophenyl)-1-(2,4-difluorophenyl)-1H-1,2,4-triazol-3-yl]oxy}acetate (S1-16) or {[5-(4-
 chloro-2-fluorophenyl)-1-(2,4-difluorophenyl)-1H-1,2,4-triazol-3-yl]oxy}acetic acid (S1-17) or
 10 methyl-1-1-(4-chloro-2-fluorophenyl)-5-(2,4-difluorophenyl)-1H-1,2,4-triazol-3-yl]oxy}acetate
 (S1-18) or {[1-(4-chloro-2-fluorophenyl)-5-(2,4-difluorophenyl)-1H-1,2,4-triazol-3-
 yl]oxy}acetic acid (S1-19), as described in patent application WO2021105101.
- S2) Compounds from the group of the 8-quinolinoxy derivatives (S2):
- 15 S2^a) Compounds of the 8-quinolinoxyacetic acid type (S2^a), preferably 1-methylhexyl (5-chloro-8-
 quinolinoxy)acetate ("cloquintocet-mexyl") (S2-1), 1,3-dimethylbut-1-yl (5-chloro-8-
 quinolinoxy)acetate (S2-2), 4-allyloxybutyl (5-chloro-8-quinolinoxy)acetate (S2-3), 1-
 allyloxyprop-2-yl (5-chloro-8-quinolinoxy)acetate (S2-4), ethyl (5-chloro-8-quinolinoxy)acetate
 (S2-5), methyl (5-chloro-8-quinolinoxy)acetate (S2-6), allyl (5-chloro-8-quinolinoxy)acetate
 20 (S2-7), 2-(2-propylideneiminoxy)-1-ethyl (5-chloro-8-quinolinoxy)acetate (S2-8), 2-oxoprop-1-
 yl (5-chloro-8-quinolinoxy)acetate (S2-9) and related compounds, as described in EP-A-86750,
 EP-A-94349 and EP-A-191736 or EP-A-0 492 366, and also (5-chloro-8-quinolinoxy)acetic acid
 (S2-10), hydrates and salts thereof, for example the lithium, sodium, potassium, calcium,
 magnesium, aluminium, iron, ammonium, quaternary ammonium, sulfonium or phosphonium
 25 salts thereof, as described in WO-A-2002/34048;
- S2^b) Compounds of the (5-chloro-8-quinolinoxy)malonic acid type (S2^b), preferably compounds such
 as diethyl (5-chloro-8-quinolinoxy)malonate, diallyl (5-chloro-8-quinolinoxy)malonate, methyl
 ethyl (5-chloro-8-quinolinoxy)malonate and related compounds, as described in EP-A-0 582
 198.
- 30 S3) Active ingredients of the dichloroacetamide type (S3), which are frequently used as pre-
 emergence safeners (soil-acting safeners), for example
 "dichlormid" (N,N-diallyl-2,2-dichloroacetamide) (S3-1),
 "R-29148" (3-dichloroacetyl-2,2,5-trimethyl-1,3-oxazolidine) from Stauffer (S3-2),
 "R-28725" (3-dichloroacetyl-2,2-dimethyl-1,3-oxazolidine) from Stauffer (S3-3),
 35 "benoxacor" (4-dichloroacetyl-3,4-dihydro-3-methyl-2H-1,4-benzoxazine) (S3-4),
 "PPG-1292" (N-allyl-N-[(1,3-dioxolan-2-yl)methyl]dichloroacetamide) from PPG Industries
 (S3-5),

"DKA-24" (N-allyl-N-[(allylaminocarbonyl)methyl]dichloroacetamide) from Sagro-Chem (S3-6),

"AD-67" or "MON 4660" (3-dichloroacetyl-1-oxa-3-azaspiro[4.5]decane) from Nitrokemia or Monsanto (S3-7),

5 "TI-35" (1-dichloroacetylazepane) from TRI-Chemical RT (S3-8),

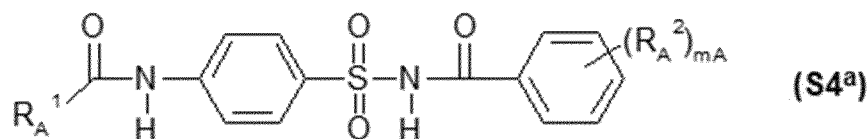
"diclonon" (dicyclonon) or "BAS145138" or "LAB145138" (S3-9)

((RS)-1-dichloroacetyl-3,3,8a-trimethylperhydropyrrolo[1,2-a]pyrimidin-6-one) from BASF,

"furilazole" or "MON 13900" ((RS)-3-dichloroacetyl-5-(2-furyl)-2,2-dimethyloxazolidine) (S3-10), and the (R) isomer thereof (S3-11).

10 S4) Compounds from the class of the acylsulfonamides (S4):

S4^a) N-Acylsulfonamides of the formula (S4^a) and salts thereof, as described in WO-A-97/45016,



in which

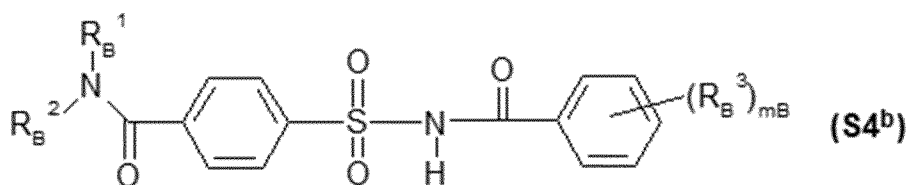
R_A¹ is (C₁-C₆)-alkyl, (C₃-C₆)-cycloalkyl, where the 2 latter radicals are substituted by v_A substituents from the group of halogen, (C₁-C₄)-alkoxy, (C₁-C₆)-haloalkoxy and (C₁-C₄)-alkylthio and, in the case of cyclic radicals, also by (C₁-C₄)-alkyl and (C₁-C₄)-haloalkyl;

R_A² is halogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, CF₃;

m_A is 1 or 2;

v_A is 0, 1, 2 or 3;

20 S4^b) Compounds of the 4-(benzoylsulfamoyl)benzamide type of the formula (S4^b) and salts thereof, as described in WO-A-99/16744,



in which

R_B¹, R_B² are independently hydrogen, (C₁-C₆)-alkyl, (C₃-C₆)-cycloalkyl, (C₃-C₆)-alkenyl, (C₃-C₆)-alkynyl,

R_B³ is halogen, (C₁-C₄)-alkyl, (C₁-C₄)-haloalkyl or (C₁-C₄)-alkoxy and

m_B is 1 or 2,

e.g. those in which

R_B¹ = cyclopropyl, R_B² = hydrogen and (R_B³) = 2-OMe ("cyprosulfamide", S4-1),

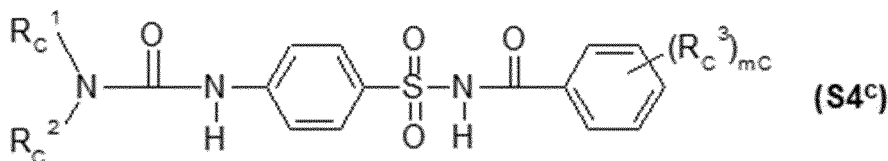
30 R_B¹ = cyclopropyl, R_B² = hydrogen and (R_B³) = 5-Cl-2-OMe (S4-2),

R_B¹ = ethyl, R_B² = hydrogen and (R_B³) = 2-OMe (S4-3),

R_B^1 = isopropyl, R_B^2 = hydrogen and (R_B^3) = 5-Cl-2-OMe (S4-4) and

R_B^1 = isopropyl, R_B^2 = hydrogen and (R_B^3) = 2-OMe (S4-5);

- S4^c) Compounds from the class of the benzoylsulfamoylphenylureas of the formula (S4^c), as described in EP-A-365484,



in which

R_C^1 , R_C^2 are independently hydrogen, (C₁-C₈)-alkyl, (C₃-C₈)-cycloalkyl, (C₃-C₆)-alkenyl, (C₃-C₆)-alkynyl,

R_C^3 is halogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, CF₃, and

m_C is 1 or 2;

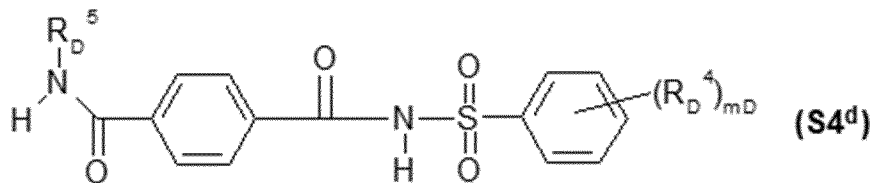
for example

1-[4-(N-2-methoxybenzoylsulfamoyl)phenyl]-3-methylurea,

1-[4-(N-2-methoxybenzoylsulfamoyl)phenyl]-3,3-dimethylurea,

1-[4-(N-4,5-dimethylbenzoylsulfamoyl)phenyl]-3-methylurea;

- S4^d) Compounds of the N-phenylsulfonylterephthalamide type of the formula (S4^d) and salts thereof, which are known, for example, from CN 101838227,



in which

R_D^4 is halogen, (C₁-C₄)-alkyl, (C₁-C₄)-alkoxy, CF₃;

m_D is 1 or 2;

R_D^5 is hydrogen, (C₁-C₆)-alkyl, (C₃-C₆)-cycloalkyl, (C₂-C₆)-alkenyl, (C₂-C₆)-alkynyl, (C₅-C₆)-cycloalkenyl.

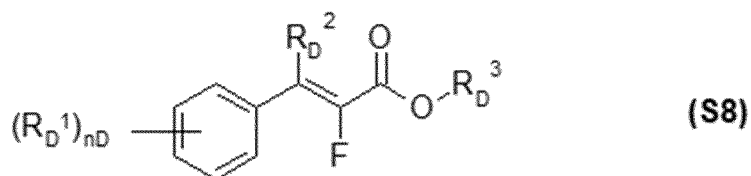
- S5) Active ingredients from the class of the hydroxyaromatics and the aromatic-aliphatic carboxylic acid derivatives (S5), for example ethyl 3,4,5-triacetoxybenzoate, 3,5-dimethoxy-4-hydroxybenzoic acid, 3,5-dihydroxybenzoic acid, 4-hydroxysalicylic acid, 4-fluorosalicylic acid, 2-hydroxycinnamic acid, 2,4-dichlorocinnamic acid, as described in WO-A-2004/084631, WO-A-2005/015994, WO-A-2005/016001.

- S6) Active ingredients from the class of the 1,2-dihydroquinoxalin-2-ones (S6), for example 1-methyl-3-(2-thienyl)-1,2-dihydroquinoxalin-2-one, 1-methyl-3-(2-thienyl)-1,2-dihydroquinoxaline-2-thione, 1-(2-aminoethyl)-3-(2-thienyl)-1,2-dihydroquinoxalin-2-one

hydrochloride, 1-(2-methylsulfonylaminoethyl)-3-(2-thienyl)-1,2-dihydroquinoxalin-2-one, as described in WO-A-2005/112630.

S7) Compounds from the class of the diphenylmethoxyacetic acid derivatives (S7), e.g. methyl diphenylmethoxyacetate (CAS Reg. No. 41858-19-9) (S7-1), ethyl diphenylmethoxyacetate or diphenylmethoxyacetic acid, as described in WO-A-98/38856.

S8) Compounds of the formula (S8), as described in WO-A-98/27049,



in which the symbols and indices are defined as follows:

R_D^1 is halogen, (C₁-C₄)-alkyl, (C₁-C₄)-haloalkyl, (C₁-C₄)-alkoxy, (C₁-C₄)-haloalkoxy,

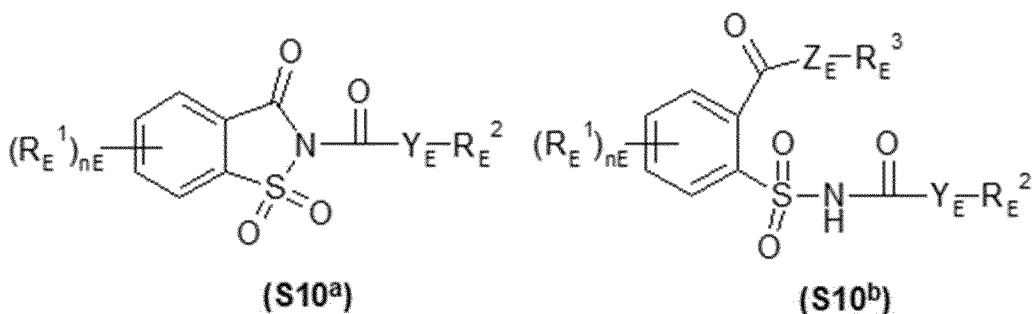
R_D^2 is hydrogen or (C₁-C₄)-alkyl,

R_D^3 is hydrogen, (C₁-C₈)-alkyl, (C₂-C₄)-alkenyl, (C₂-C₄)-alkynyl or aryl, where each of the aforementioned carbon-containing radicals is unsubstituted or substituted by one or more, preferably up to three, identical or different radicals from the group consisting of halogen and alkoxy; or salts thereof,

n_D is an integer from 0 to 2.

S9) Active ingredients from the class of the 3-(5-tetrazolylcarbonyl)-2-quinolones (S9), for example 1,2-dihydro-4-hydroxy-1-ethyl-3-(5-tetrazolylcarbonyl)-2-quinolone (CAS Reg. No.: 219479-18-2), 1,2-dihydro-4-hydroxy-1-methyl-3-(5-tetrazolylcarbonyl)-2-quinolone (CAS Reg. No. 95855-00-8), as described in WO-A-1999/000020.

S10) Compounds of the formulae (S10^a) or (S10^b) as described in WO-A-2007/023719 and WO-A-2007/023764



in which

R_E^1 is halogen, (C₁-C₄)-alkyl, methoxy, nitro, cyano, CF₃, OCF₃,

Y_E, Z_E are independently O or S,

n_E is an integer from 0 to 4,

R_E^2 is (C₁-C₁₆)-alkyl, (C₂-C₆)-alkenyl, (C₃-C₆)-cycloalkyl, aryl; benzyl, halobenzyl,

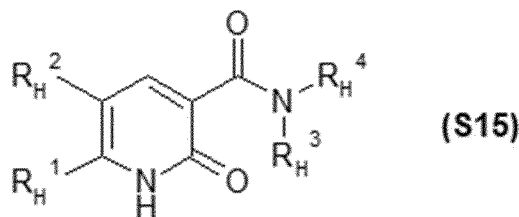
R_E^3 is hydrogen or (C₁-C₆)-alkyl.

- S11) Active ingredients of the oxyimino compounds type (S11), which are known as seed-dressing agents, for example
 "oxabetrinil" ((Z)-1,3-dioxolan-2-ylmethoxyimino(phenyl)acetonitrile) (S11-1), which is known as a seed-dressing safener for millet/sorghum against metolachlor damage,
 5 "fluxofenim" (1-(4-chlorophenyl)-2,2,2-trifluoro-1-ethanone O-(1,3-dioxolan-2-ylmethyl)-oxime) (S11-2), which is known as a seed-dressing safener for millet/sorghum against metolachlor damage, and
 "cyometrinil" or "CGA-43089" ((Z)-cyanomethoxyimino(phenyl)acetonitrile) (S11-3), which is known as a seed-dressing safener for millet/sorghum against metolachlor damage.
- 10 S12) Active ingredients from the class of the isothiochromanones (S12), for example methyl [(3-oxo-1H-2-benzothiopyran-4(3H)-ylidene)methoxy]acetate (CAS Reg. No. 205121-04-6) (S12-1) and related compounds from WO-A-1998/13361.
- S13) One or more compounds from group (S13):
 "naphthalic anhydride" (1,8-naphthalenedicarboxylic anhydride) (S13-1), which is known as a
 15 seed-dressing safener for maize against thiocarbamate herbicide damage,
 "fenclorim" (4,6-dichloro-2-phenylpyrimidine) (S13-2), which is known as a safener for pretilachlor in sown rice,
 "flurazole" (benzyl 2-chloro-4-trifluoromethyl-1,3-thiazole-5-carboxylate) (S13-3), which is known as a seed-dressing safener for millet/sorghum against alachlor and metolachlor damage,
 20 "CL 304415" (CAS Reg. No. 31541-57-8)
 (4-carboxy-3,4-dihydro-2H-1-benzopyran-4-acetic acid) (S13-4) from American Cyanamid, which is known as a safener for maize against damage by imidazolinones,
 "MG 191" (CAS Reg. No. 96420-72-3) (2-dichloromethyl-2-methyl-1,3-dioxolane) (S13-5) from Nitrokemia, which is known as a safener for maize,
 25 "MG 838" (CAS Reg. No. 133993-74-5)
 (2-propenyl 1-oxa-4-azaspiro[4.5]decane-4-carbodithioate) (S13-6) from Nitrokemia
 "disulfoton" (O,O-diethyl S-2-ethylthioethyl phosphorodithioate) (S13-7),
 "dietholate" (O,O-diethyl O-phenyl phosphorothioate) (S13-8),
 "mephenate" (4-chlorophenyl methylcarbamate) (S13-9).
- 30 S14) Active ingredients which, in addition to herbicidal action against harmful plants, also have safener action on crop plants such as rice, for example
 "dimepiperate" or "MY-93" (S-1-methyl 1-phenylethylpiperidine-1-carbothioate), which is known as a safener for rice against damage by the herbicide molinate,
 "daimuron" or "SK 23" (1-(1-methyl-1-phenylethyl)-3-p-tolylurea), which is known as a safener
 35 for rice against damage by the herbicide imazosulfuron,
 "cumyluron" = "JC-940" (3-(2-chlorophenylmethyl)-1-(1-methyl-1-phenylethyl)urea, see JP-A-60087254), which is known as a safener for rice against damage by some herbicides,

"methoxyphenone" or "NK 049" (3,3'-dimethyl-4-methoxybenzophenone), which is known as a safener for rice against damage by some herbicides,

"CSB" (1-bromo-4-(chloromethylsulfonyl)benzene) from Kumiai, (CAS Reg. No. 54091-06-4), which is known as a safener against damage by some herbicides in rice.

5 S15) Compounds of the formula (S15) or tautomers thereof



as described in WO-A-2008/131861 and WO-A-2008/131860

in which

10 R_H^1 is a (C₁-C₆)-haloalkyl radical and

R_H^2 is hydrogen or halogen and

R_H^3 , R_H^4 are independently hydrogen, (C₁-C₁₆)-alkyl, (C₂-C₁₆)-alkenyl or (C₂-C₁₆)-alkynyl, where

each of the 3 latter radicals is unsubstituted or substituted by one or more radicals from

the group of halogen, hydroxyl, cyano, (C₁-C₄)-alkoxy, (C₁-C₄)-haloalkoxy, (C₁-C₄)-

15 alkylthio, (C₁-C₄)-alkylamino, di[(C₁-C₄)-alkyl]amino, [(C₁-C₄)-alkoxy]carbonyl, [(C₁-

C₄)-haloalkoxy]carbonyl, (C₃-C₆)-cycloalkyl which is unsubstituted or substituted,

phenyl which is unsubstituted or substituted, and heterocyclyl which is unsubstituted or substituted,

or (C₃-C₆)-cycloalkyl, (C₄-C₆)-cycloalkenyl, (C₃-C₆)-cycloalkyl fused on one side of the

20 ring to a 4 to 6-membered saturated or unsaturated carbocyclic ring, or (C₄-C₆)-

cycloalkenyl fused on one side of the ring to a 4 to 6-membered saturated or unsaturated carbocyclic ring, and

where each of the 4 latter radicals is unsubstituted or substituted by one or more radicals

from the group of halogen, hydroxyl, cyano, (C₁-C₄)-alkyl, (C₁-C₄)-haloalkyl, (C₁-C₄)-

25 alkoxy, (C₁-C₄)-haloalkoxy, (C₁-C₄)-alkylthio, (C₁-C₄)-alkylamino, di[(C₁-C₄)-

alkyl]amino, [(C₁-C₄)-alkoxy]carbonyl, [(C₁-C₄)-haloalkoxy]carbonyl, (C₃-C₆)-cycloalkyl

which is unsubstituted or substituted, phenyl which is unsubstituted or substituted, and

heterocyclyl which is unsubstituted or substituted,

or

30 R_H^3 is (C₁-C₄)-alkoxy, (C₂-C₄)-alkenyloxy, (C₂-C₆)-alkynyloxy or (C₂-C₄)-haloalkoxy and

R_H^4 is hydrogen or (C₁-C₄)-alkyl or

R_H^3 and R_H^4 together with the directly attached nitrogen atom represent a four- to eight-

membered heterocyclic ring which, as well as the nitrogen atom, may also contain

further ring heteroatoms, preferably up to two further ring heteroatoms from the group of N, O and S, and which is unsubstituted or substituted by one or more radicals from the group of halogen, cyano, nitro, (C₁-C₄)-alkyl, (C₁-C₄)-haloalkyl, (C₁-C₄)-alkoxy, (C₁-C₄)-haloalkoxy and (C₁-C₄)-alkylthio.

- 5 S16) Active ingredients which are used primarily as herbicides but also have safener action on crop plants, for example
 (2,4-dichlorophenoxy)acetic acid (2,4-D),
 (4-chlorophenoxy)acetic acid,
 (R,S)-2-(4-chloro-o-tolyloxy)propionic acid (mecoprop),
 10 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB),
 (4-chloro-o-tolyloxy)acetic acid (MCPA),
 4-(4-chloro-o-tolyloxy)butyric acid,
 4-(4-chlorophenoxy)butyric acid,
 3,6-dichloro-2-methoxybenzoic acid (dicamba),
 15 1-(ethoxycarbonyl)ethyl 3,6-dichloro-2-methoxybenzoate (lactidichlor-ethyl).

Preferred safeners in combination with the herbicide combinations of the invention are: cloquintocet-mexyl, cyprosulfamide, fenchlorazole ethyl ester, isoxadifen-ethyl, mefenpyr-diethyl, fenclorim, cumyluron, S4-1 and S4-5, and particularly preferred safeners are: cloquintocet-mexyl, cyprosulfamide,
 20 isoxadifen-ethyl and mefenpyr-diethyl.

The one or more agrochemically active ingredients g) different from a) and f) may be selected from diflufenican, pyroxasulfone, metribuzin, mesotrione, aclonifen, bromoxynil, bromoxynil-butyrate, -potassium, -heptanoate, and -octanoate, benzofenap, butachlor, 2,4-D, 2,4-D-butotyl-, butyl-, -dimethylammonium, -diolamin, -ethyl, -2-ethylhexyl, -isobutyl, -isooctyl, -isopropylammonium, -
 25 potassium, -triisopropanolammonium, and -trolamine, diflufenican, dimethenamid, ethoxysulfuron, fenoxaprop, fenoxaprop-P, fenoxaprop-ethyl, fenoxaprop-P-ethyl, fenquinothione, fentrazamide, florasulam, flufenacet, fluroxypyr, fluroxypyr-meptyl, foramsulfuron, iodosulfuron, iodosulfuron-methyl-sodium, isoproturon, isoxaflutole, mefenacet, mesosulfuron, mesosulfuron-methyl, metolachlor, S-metolachlor, metribuzin, metosulam, nicosulfuron, oxadiargyl, oxadiazon, pethoxamid, prosulfocarb,
 30 pyrasulfotole, pyroxulam, tefuryltrione, tembotrione, triafamone, pendimethalin, propoxycarbazone, halauxifen-methyl, 2-methyl-4-chlorophenoxyacetic acid (MCPA).

Preferably, the further agrochemically active ingredient is fluroxypyr-meptyl.

The emulsifiable concentrate formulation may further comprise common adjuvants and additives h) known in the art and compatible with agrochemical formulations. Such additives may be for example

stabilizers, such as antifreeze, preservatives, antioxidants, light stabilizers, in particular UV stabilizers, other agents which improve chemical and/or physical stability.

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

Other additives are penetration enhancers, such as ethoxylated linear and/or branched fatty alcohols (e.g. Genapol® X-type of Clariant) with 2-20 EO units; methyl end-capped, ethoxylated linear and/or branched fatty alcohols (e.g. Genapol® XM-type of Clariant) comprising 2-20 EO units; ethoxylated coconut
10 alcohols (e.g. Genapol® C-types of Clariant) comprising 2-20 EO units; ethoxylated C12/15 alcohols (e.g. Synperonic® A-types of Croda) comprising 2-20 EO units; propoxy-ethoxylated alcohols, branched or linear, e.g. Antarox® B/848 of Solvay, Atlas® G5000 of Croda, Lucramul® HOT 5902 of Levaco, Break-Thru Vibrant of Evonik; propoxy-ethoxylated fatty acids, Me end-capped, e.g. Leofat® OC0503M of Lion; alkyl ether citrate surfactants (e.g. Adsee CE range, Akzo Nobel); alkylpolysaccharides (e.g.
15 Agnique® PG8107, PG8105 of BASF; Atplus® 438, AL-2559, AL-2575 of Croda); ethoxylated mono- or diesters of glycerine comprising fatty acids with 8-18 carbon atoms and an average of 10-40 EO units (e.g. Crovol® product range of Croda); castor oil ethoxylates comprising an average of 5-40 EO units (e.g. Berol® range of Nouryon, Emulsogen® EL range of Clariant); block-copolymer of polyethylene oxide and polypropylene oxide (e.g. Pluronic range of BASF).

20 Other additives are wetting agents, spreading agents, retention agents, such as ethoxylated branched alcohols (e.g. Genapol® X-type) with 2-20 EO units; methyl end-capped, ethoxylated branched alcohols (e.g. Genapol® XM-type) comprising 2-20 EO units; propoxy-ethoxylated alcohols, branched or linear, e.g. Antarox® B/848, Atlas® G5000, Lucramul® HOT 5902; organomodified polysiloxanes, e.g. BreakThru® OE444, BreakThru® S240, Silwett® L77, Silwet 312, Silwett® 408, Silwet® 806; mono-
25 and diesters of sulfosuccinate Na salts with branched or linear alcohols comprising 1-10 carbon atoms, e.g. Geropon DOS; ethoxylated diacetylene-diols, e.g. Surfynol® 4xx-range.

Suitable adjuvants, which typically function as uptake enhancers, are oils, such as sunflower oil, rapeseed oil, corn oil, soybean oil, rice bran oil, olive oil; ethylhexyl oleate, ethylhexyl palmitate, ethylhexyl myristate/laurate, ethylhexyl laurate, ethylhexyl caprylate/caprinate, iso-propyl myristate, iso-propyl
30 palmitate, methyl oleate, methyl palmitate, ethyl oleate, rape seed oil methyl ester, soybean oil methyl ester, rice bran oil methyl ester, mineral oils, e.g. Exxsol® D100, Solvesso® 200ND. The adjuvant may also be selected from tris-alkyl-phosphate esters, preferably tris (2-ethylhexyl) phosphate, e.g. Disflamoll® TOF.

The adjuvant may also be selected from the following group of compounds: ethoxylated branched alcohols (e.g. Genapol® X-type) with 2-20 EO units; methyl end-capped, ethoxylated branched alcohols (e.g. Genapol® XM-type) comprising 2-20 EO units; ethoxylated coconut alcohols (e.g. Genapol® C-types) comprising 2-20 EO units; ethoxylated C12/15 alcohols (e.g. Synperonic® A-types) comprising 2-20 EO units; propoxy-ethoxylated alcohols, branched or linear, e.g. Antaro® B/848, Atlas® G5000, Lucramul® HOT 5902; propoxy-ethoxylated fatty acids, Me end-capped, e.g. Leofat® OC0503M; alkyl ether citrate surfactants (e.g. Adsee® CE range, Akzo Nobel); i. ethoxylated mono- or diesters of glycerine comprising fatty acids with 8-18 carbon atoms and an average of 10-40 EO units (e.g. Crovol® range); castor oil ethoxylates comprising an average of 5-40 EO units (e.g. Berol® range, Emulsogen® EL range); ethoxylated oleic acid (e.g. Alkamuls® A and AP) comprising 2-20 EO units; ethoxylated sorbitan fatty acid esters comprising fatty acids with 8-18 carbon atoms and an average of 10-50 EO units (e.g. Arlatone® T, Tween range).

Preferred uptake enhancers according to the present invention are tris (2-ethylhexyl) phosphate, rapeseed oil methyl esters, ethoxylated coconut alcohols, propoxy-ethoxylated alcohols and mineral oils.

The herbicidal compositions have outstanding herbicidal activity against a broad spectrum of economically important monocotyledonous and dicotyledonous harmful plants. Even perennial weeds which produce shoots from rhizomes, rootstocks or other perennial organs and which are difficult to control are controlled well. In this context, it does not matter whether the herbicidal compositions are applied before sowing, pre-emergence or post-emergence. Specific examples may be mentioned of some representatives of the monocotyledonous and dicotyledonous weed flora which can be controlled by the herbicidal compositions, without the enumeration being a restriction to certain species.

Examples of weed species on which the herbicidal compositions act efficiently are, from amongst the monocotyledonous weed species, *Apera spica venti*, *Avena* spp., *Alopecurus* spp., *Brachiaria* spp., *Digitaria* spp., *Lolium* spp., *Echinochloa* spp., *Panicum* spp., *Phalaris* spp., *Poa* spp., *Setaria* spp. and *Bromus* spp. such as *Bromus catharticus*, *Bromus secalinus*, *Bromus erectus*, *Bromus tectorum* and *Bromus japonicus*, and *Cyperus* species from the annual group, and, among the perennial species, *Agropyron*, *Cynodon*, *Imperata* and *Sorghum* and also perennial *Cyperus* species. In the case of the dicotyledonous weed species, the spectrum of action extends to genera such as, for example, *Abutilon* spp., *Amaranthus* spp., *Chenopodium* spp., *Chrysanthemum* spp., *Galium* spp. such as *Galium aparine*, *Ipomoea* spp., *Kochia* spp., *Lamium* spp., *Matricaria* spp., *Pharbitis* spp., *Polygonum* spp., *Sida* spp., *Sinapis* spp., *Solanum* spp., *Stellaria* spp., *Veronica* spp. and *Viola* spp., *Xanthium* spp., among the annuals, and *Convolvulus*, *Cirsium*, *Rumex* and *Artemisia* in the case of the perennial weeds.

The herbicidal compositions also act outstandingly efficiently on harmful plants which are found under the specific culture conditions in rice, such as, for example, Echinochloa, Sagittaria, Alisma, Eleocharis, Scirpus and Cyperus.

5 If the herbicidal compositions are applied to the soil surface before germination, the weed seedlings are either prevented completely from emerging or else the weeds grow until they have reached the cotyledon stage, but then their growth stops, and, eventually, after three to four weeks have elapsed, they die completely.

10 If the herbicidal compositions are applied post-emergence to the green parts of the plants, growth likewise stops drastically a very short time after the treatment, and the weed plants remain at the growth stage of the point of time of application, or they die completely after a certain time, so that in this manner competition by the weeds, which is harmful to the crop plants, is eliminated very early and in a sustained manner.

The herbicidal compositions are distinguished by a rapidly commencing and long-lasting herbicidal action. As a rule, the rainfastness of the active substances in the herbicidal compositions is advantageous.
15 A particular advantage is that the dosages used in the herbicidal compositions and the effective dosages of herbicidal compounds can be adjusted to such a low level that their soil action is optimally low. This does not only allow them to be employed in sensitive crops in the first place, but groundwater contaminations are virtually avoided. The active compound combination according to the invention allows the required application rate of the active substances to be reduced considerably.

20 The abovementioned properties and advantages are necessary for weed control practice to keep agricultural crops free from undesired competing plants, and thus to ensure and/or increase yield levels from the qualitative and quantitative angle. These novel herbicidal compositions markedly exceed the technical state of the art with a view to the properties described.

25 While the herbicidal compositions have an outstanding herbicidal activity against monocotyledonous and dicotyledonous weeds, crop plants of economically important crops, for example dicotyledonous crops such as soya, cotton, oilseed rape, sugarbeet, or graminaceous crops such as wheat, barley, rye, oats, millet, rice or corn, are damaged only to a minor extent, if at all. This is why the present herbicidal compositions are highly suitable for the selective control of undesired plant growth in plantations of agricultural crops or of ornamentals.

30 Owing to their herbicidal properties, the herbicidal compositions can also be employed for controlling harmful plants in crops of genetically modified plants which are known or yet to be developed. As a rule, the recombinant plants are distinguished by specific advantageous characteristics, for example by resistances to certain pesticides, in particular certain herbicides, resistances to plant diseases or the

causative organisms of plant diseases such as specific insects or microorganisms such as fungi, bacteria or viruses. Other specific characteristics relate, for example, to the harvested material with regard to quantity, quality, storability, composition and specific constituents. Thus, for example, transgenic plants are known whose starch content is increased, or whose starch quality is altered, or those where the harvested material has a different fatty acid composition.

The use of the herbicidal compositions in economically important transgenic crops of useful plants and ornamentals, for example of graminaceous crops such as wheat, barley, rye, oats, millet, rice and corn, or else crops of sugarbeet, cotton, soya, oilseed rape, potatoes, tomatoes, peas and other vegetables, is preferred. Preferably, the herbicidal compositions can be employed in crops of useful plants which resist the phytotoxic effects of the herbicides, or have been made to resist these effects by recombinant techniques.

When using the herbicidal compositions in transgenic crops, effects are frequently observed in addition to the effects against harmful plants to be observed in other crops, which are specific for the application in the transgenic crop in question, for example a modified or specifically widened weed spectrum which can be controlled, modified application rates which may be employed for application, preferably good combining ability with the further herbicidally active compounds to which the transgenic crop is resistant, and an effect on growth and yield level of the transgenic crop plants.

The present invention therefore also relates to a method for controlling undesired vegetation (harmful plants), preferably in crops of plants such as cereals (for example wheat, barley, rye, oats, rice, corn and millet), sugar beet, sugar cane, oilseed rape, cotton and soya, especially preferably in monocotyledonous plants such as cereals, for example wheat, barley, rye, oats, and their hybrids such as triticale, rice, corn and millet, wherein the formulations according to the invention or the herbicidal compositions obtainable therefrom are applied to the harmful plants, plant parts, seeds of the plants or the area on which the plants grow, for example the area under cultivation, in an effective amount.

The plant crops may also be genetically modified or have been obtained by mutation selection; they preferably tolerate acetolactate synthase (ALS) inhibitors.

The plants treated according to the invention are, as far as the use of herbicides is concerned, all types of harmful plants, such as weeds. With respect to the protection of crop plants by application of, for example, fungicides and insecticides, the use in economically important crops including, for example, also transgenic crops, of useful plants and ornamentals, for example of cereals, such as wheat, barley, rye, oats, millet, rice, manioc and corn, or else crops of peanut, sugar beet, cotton, soybean, oilseed rape, potato, tomato, pea and other vegetable species, is preferred.

The process for preparing the formulations according to the invention can be chosen from a number of processes known per se which describe the preparation of emulsifiable concentrates.

- The formulations according to the invention have excellent chemical and physical stability during preparation and storage and are suitable in particular also for combinations of active compounds having different physicochemical properties. Overall, the formulations according to the invention have the long-term storage stability desired and are without fault from a technical point of view.

Examples

The examples are meant to illustrate the invention and do not limit it to the processes and compounds described therein.

Starting materials:

The compounds used in the examples are hereafter specified in Table 1.

Table 1: Chemicals used in the examples.

Fluroxypyr-Meptyl (Bayer)	Herbicide; CAS 81406-37-3
Thiencarbazone-Methyl (Bayer)	Herbicide; CAS 317815-83-1
Mefenpyr-Diethyl (Bayer)	Safener; CAS 135590-91-9
Genamin S 080 (Clariant)	Organic base; Stearylamine ethoxylate (Stearylamine with 8 mole ethylene oxide)
Genamin C 050 (Clariant)	Organic base; Amine ethoxylate based on cocos fatty amine
Triethanolamine	Organic base; CAS 102-71-6
Propylene Carbonate	Water-miscible solvent; CAS 108-32-7
Dimethylformamide	Water-miscible solvent; CAS 68-12-2
Dimethylsulfoxid	Water-miscible solvent; CAS 67-68-5
Glycerol-1,2-carbonate	Water-miscible solvent; CAS 931-40-8
N-Methylpyrrolidone	Water-miscible solvent; CAS 872-50-4
Steposol EA (Stepan)	Water-miscible solvent; Acetamid, N-[2-(acetyloxy)ethyl]-N-methyl
Rapeseed Oil Methyl Ester (RME)	Water-immiscible solvent
Rhodacal 60 BE (Solvay)	Anionic emulsifier; linear Calcium dodecylbenzene sulfonate, 60% active
Triton GR 7 ME (Dow)	Anionic emulsifier; Sulfosuccinate
Soprophor 796/P (Solvay)	Nonionic emulsifier; Tristyrylphenol-Alkoxylate
Emulsogen EL 400 (Clariant)	Emulsifier; Castor Oil, ethoxylated (40 EO)
Genapol X 090 (Clariant)	Nonionic emulsifier; Isotridecanol Ethoxylates 9EO
Solvesso 200 (Exxon)	Superheavy aromatic water- immiscible solvent

Example 1:

Emulsifiable concentrate formulations according to Table 2 below were prepared by first mixing all liquid components followed by adding the solid components to the mixture and eventually heating to 30 to 60 °C. In these formulations, different organic water-miscible solvents were tested, namely propylene carbonate, glycerol-1,2-carbonate, dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone and Acetamid, N-[2-(acetyloxy)ethyl)]-N-methyl (Steposol EA).

The formulations were tested for stability at 54°C after two weeks by measuring the content of thiencarbazone-methyl via HPLC. The chemical degradation (%) in the below table 2 shows the relative loss of thiencarbazone-methyl compared to the initial amount (day 0).

10

Table 2: EC formulation examples.

Example	#1	#2	#3	#4	#5	#6
Mefenpyr-Diethyl (%w/w)	2.78	2.78	2.78	2.78	2.78	2.78
Thiencarbazone-Methyl (%w/w)	0.46	0.46	0.46	0.46	0.46	0.46
Rhodacal 60 BE (%w/w)	4	4	4	4	4	4
Soprophor 796/P (%w/w)	4	4	4	4	4	4
Genapol X 090 (%w/w)	10	10	10	10	10	10
Rapeseed Oil Methyl Ester (%w/w)	10	10	10	10	10	10
Genamin S 080 (%w/w)	1	1	1	1	1	1
Propylene Carbonate (%w/w)	25	-	-	-	-	-
Dimethylformamide (%w/w)	-	25	-	-	-	-
Dimethylsulfoxide (%w/w)	-	-	25	-	-	-
Glycerol-1,2-carbonate (%w/w)	-	-	-	25	-	-
N-Methylpyrrolidone (%w/w)	-	-	-	-	25	-
Steposol EA (%w/w)	-	-	-	-	-	25
Solvesso 200 (%w/w)	42.76	42.76	42.76	42.76	42.76	42.76
Chemical degradation (%) Thiencarbazone-methyl after 2 weeks at 54°C	-6.98	-28.26	-63.64	-11.63	-31.11	-29.79

While propylene carbonate and glycerol-1,2-carbonate result in an improved stability of the formulation after two weeks storage at 54 °C, in particular propylene carbonate with a degradation of only 6.98 % (indicated as “-6.98”), the other tested polar aprotic solvents dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone, and Steposol EA (Acetamid, N-[2-(acetyloxy)ethyl]-N-methyl) provide for an insufficient stability after 2 weeks storage at 54 °C, with a loss of thien carbazole-methyl of up to 63.64 % compared to the initial thien carbazole-methyl content measured directly after preparation of the formulation (= day 0).

Example 2:

Further EC formulations were prepared as described above for Example 1, but with the ingredients according to the following table 3, and tested for chemical stability of thien carbazole-methyl as described in Example 1.

Table 3: Further EC formulation examples.

Example	#7*	#8	#9	#10	#11	#12	#13	#14
Fluoroxypyr-Meptyl (%w/w)	15.63	15.63	15.63	15.63	15.63	15.63	15.63	15.63
Thien carbazole-Methyl (%w/w)	0.46	0.46	0.46	0.46	0.46	0.46	0.46	0.46
Mefenpyr-Diethyl (%w/w)	2.78	2.78	2.78	2.78	2.78	2.78	2.78	2.78
Genamin S 080 (%w/w)	0	1	1	0	0	1	0	0
Genamin C 050 (%w/w)	0	0	0	1	1	0	1	0
Triethanolamin (%w/w)	0	0	0	0	0	0	0	0.1
Rhodacal 60 BE (%w/w)	4	4	4	4	4	0	0	4
Triton GR 7ME (%w/w)	0	0	0	0	0	4	4	0
Soprophor 796/P (%w/w)	4	4	0	0	4	4	4	4
Castor Oil-40 EO (%w/w)	0	0	4	4	0	0	0	0
Rapeseed Oil Methyl Ester Syskem (%w/w)	10	10	10	10	10	10	10	10
Genapol X 090 (%w/w)	10	10	10	10	10	10	10	10

Example	#7*	#8	#9	#10	#11	#12	#13	#14
Propylene Carbonate (%w/w)	28.85	28.85	28.85	28.85	28.85	28.85	28.85	28.85
Solvesso 200 (%w/w)	23.28	23.28	23.28	23.28	23.28	23.28	23.28	23.28
pH	pH < 5	pH 6-8	pH 6-8	pH 6-8	pH 6-8	pH 6-8	pH 6-8	pH 6-8
Chemical degradation (%) Thiencarbazone-methyl after 2 weeks at 54°C	High degradation (more than 10% loss)	Low degradation (less than 10% loss)	Low degradation (less than 10% loss)	Low degradation (less than 10% loss)	Low degradation (less than 10% loss)	Low degradation (less than 10% loss)	Low degradation (less than 10% loss)	Low degradation (less than 10% loss)

* not according to the present invention

As can be seen from the above table, formulation #7 with a pH < 5 and no organic base provides for insufficient stability after two weeks storage at 54 °C, namely with chemical degradation of thiencarbazone-methyl of more than 10 % compared to the initial thiencarbazone-methyl content measured directly after preparation of the formulation (= day 0), while the other formulations provide for a suitable storage stability with degradation below 10 % (i.e. loss of thiencarbazone-methyl is less than 10%). The pH of the respective formulations is measured after (i) diluting the formulation in distilled water to a 10 % w/w formulation; (ii) stirring the mixture with a magnetic stirrer at 1,500 RPM for 10 minutes at 25°C; (iii) measuring the pH of the stirred mixture at 25 °C with a pH meter until the measured pH is stable for 10s. The pH is measured with a Knick pH-meter 766 (Calimatic, Knick SE 100N).

Example 3:

Further EC formulations were prepared according to the explanations in Example 1, with ingredients according to the following table 4. The pH was determined as described in Example 2.

5 Table 4: Further EC formulations examples.

Example	#15 (% w/w)	#16 (% w/w)	#17 (% w/w)
Fluroxypyr-meptyl	11.35	15.63	22.06
Thiencarbazone-methyl	0.48	0.46	0.93
Mefenpyr-diethyl	2.88	2.78	5.61
Genamin C 050	0.90	-	2.00
Genamin S 080	-	1.00	-
Rhodacal 60 BE	4.00	4.00	4.00
Soprophor 796/P	4.00	4.00	4.00
Rapeseed oil methyl ester	10.00	10.00	10.00
Genapol X 090	10.00	10.00	10.00
Propylene carbonate	28.85	28.85	28.04
Solvesso 200	27.54	23.28	13.36
pH	7.70	6 - 8	6 - 8
Chemical degradation (%) Thiencarbazone-methyl after 2 weeks at 54°C	-4.84	Low degradation (less than 10% loss)	Low degradation (less than 10% loss)

Said formulations of examples #15 to #17 provide for excellent storage stability as well as weed control after field application, such as against wild oat, green foxtail and yellow foxtail.

Claims:

1. Emulsifiable concentrate formulation comprising
 - a) thiencarbazone-methyl or an agrochemically acceptable salt thereof,
 - b) one or more organic water-immiscible solvents,
 - 5 c) one or more organic water-miscible solvents selected from linear and cyclic carbonate esters,
 - d) one or more emulsifiers,
 - e) one or more organic bases,wherein the formulation exhibits a pH of between pH 5.5 and pH 9.
- 10 2. Emulsifiable concentrate formulation according to claim 1, wherein the formulation exhibits a pH of between pH 6.0 and 8.5, preferably between pH 6.5 and 8.0, even further preferably between pH 6.8 and 7.7.
3. Emulsifiable concentrate formulation according to claim 1 or 2, wherein the pH is adjusted by
15 means of the one or more organic bases e).
4. Emulsifiable concentrate formulation according to any one of the preceding claims, wherein the one or more organic bases is selected from amine-based organic bases.
- 20 5. Emulsifiable concentrate formulation according to the preceding claim, wherein the one or more organic base is an ethoxylated amine.
6. Emulsifiable concentrate formulation according to any one of the preceding claims, wherein the one or more organic water-immiscible solvents is selected from aromatic and/or aliphatic
25 hydrocarbons.
7. Emulsifiable concentrate formulation according to any one of the preceding claims, wherein the one or more organic water-miscible solvents is selected from methyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate and isomers thereof, propylene
30 carbonate, glycerol-1,2-carbonate and butylene carbonate, or mixtures thereof.
8. Emulsifiable concentrate formulation according to the preceding claim, wherein the one or more organic water-miscible solvents is propylene carbonate.

9. Emulsifiable concentrate formulation according to any one of the preceding claims, wherein the one or more organic base is selected from amine-based organic bases and the one or more organic water-miscible solvents is selected from methyl carbonate, diethyl carbonate, dipropyl carbonate, diisopropyl carbonate, dibutyl carbonate and isomers thereof, propylene carbonate, glycerol-1,2-carbonate and butylene carbonate.
10. Emulsifiable concentrate formulation according to any one of the preceding claims, wherein the organic base is an ethoxylated amine and the organic water-miscible solvent is propylene carbonate.
11. Emulsifiable concentrate formulation according to any one of the preceding claims, further comprising one or more of the following:
- f) one or more safeners,
 - g) one or more agrochemically active ingredients different from a) and f),
 - h) further adjuvants compatible with agrochemical formulations, wetting agents and/or other additives.
12. Emulsifiable concentrate formulation according to claim 11, wherein the safener is selected from cloquintocet-mexyl, cyprosulfamide, fenclorazole ethyl ester, isoxadifen-ethyl, mefenpyr-diethyl, fenclorim, cumyluron; preferably wherein the safener is mefenpyr-diethyl.
13. Emulsifiable concentrate formulation according to any one of the preceding claims 11 or 12, wherein the one or more agrochemically active ingredients different from a) and f) is selected from diflufenican, pyroxasulfone, metribuzin, mesotrione, aclonifen, bromoxynil, bromoxynil-butyrate, -potassium, -heptanoate, and -octanoate, benzofenap, butachlor, 2,4-D, 2,4-D-butotyl-, butyl, -dimethylammonium, -diolamin, -ethyl, -2-ethylhexyl, -isobutyl, -isooctyl, -isopropylammonium, -potassium, -triisopropanolammonium, and -trolamine, diflufenican, dimethenamid, ethoxysulfuron, fenoxaprop, fenoxaprop-P, fenoxaprop-ethyl, fenoxaprop-P-ethyl, fenquinotrione, fentrazamide, florasulam, flufenacet, fluroxypyr, fluroxypyr-meptyl, foramsulfuron, iodosulfuron, iodosulfuron-methyl-sodium, isoproturon, isoxaflutole, mefenacet, mesosulfuron, mesosulfuron-methyl, metolachlor, S-metolachlor, metribuzin, metosulam, nicosulfuron, oxadiargyl, oxadiazon, pethoxamid, prosulfocarb, pyrasulfotole, pyroxsulam, tefuryltrione, tembotrione, triafamone, pendimethalin, propoxycarbazone, halauxifen-methyl, and 2-methyl-4-chlorophenoxyacetic acid (MCPA); preferably wherein the agrochemically active ingredient different from a) and f) is fluroxypyr-meptyl.

14. Emulsifiable concentrate formulation according to any one of the preceding claims, comprising
- a) 0.01 to 5 % by weight, preferably from 0.1 to 2 % by weight, further preferably 0.3 to 1 % by weight thienecarbazone-methyl or an agrochemically acceptable salt thereof,
 - b) 5 to 95 % by weight, preferably 10 to 70 % by weight, further preferably 20 to 60 % by weight of the one or more organic water-immiscible solvents,
 - c) 5 to 95 % by weight, preferably 10 to 60 % by weight, further preferably 20 to 40 % by weight of the one or more organic water-miscible solvents,
 - d) 0.1 to 30 % by weight, preferably 1 to 25 % by weight, further preferably 5 to 20 % by weight of the one or more emulsifiers,
 - e) 0.1 to 10 % by weight, preferably 0.2 to 5 % by weight, further preferably 0.5 to 2 % by weight of the organic base,
 - f) 0 to 10 % by weight, preferably 1 to 8 % by weight, further preferably 2 to 6 % by weight of one or more safeners,
 - g) 0 to 40 % by weight, preferably 5 to 30 % by weight, further preferably 10 to 25 % by weight of one or more agrochemically active ingredients different from a) and f),
 - h) 0 to 40 % by weight, preferably 5 to 30 % by weight, further preferably 10 to 20 % by weight of further adjuvants compatible with agrochemical formulations, wetting agents and/or other additives.
15. Method of combating unwanted plants at a foliar locus comprising treating the foliar locus with a composition obtained from emulsifying an emulsifiable concentrate formulation according to any one of the claims 1 to 14 in water.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/058100

A. CLASSIFICATION OF SUBJECT MATTER INV. A01N47/38 A01P13/02 A01N25/02 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) A01N A01P Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 107 926 970 A (NANJING RED SUN CO LTD) 20 April 2018 (2018-04-20) example 1 -----	1 - 15
A	US 2005/233906 A1 (SCHNABEL GERHARD [DE] ET AL) 20 October 2005 (2005-10-20) examples 1-5; table 1 -----	1 - 15
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 17 June 2024		Date of mailing of the international search report 01/07/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Davies, Maxwell

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/058100

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