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(54) Title: LIQUID HERBICIDAL PREPARATIONS

(57) Abstract: The invention is directed to a liquid herbicidal emulsifiable concentrate comprising (a) the herbicidal active substance metribuzin, (b) one or more herbicidal active substances selected from the group consisting of the ACCase inhibitors (b1), (b2) and (b3): (b1) esters of fenoxaprop-P and esters of fenoxaprop, (b2) esters of clodinafop, (b3) pinoxaden, (c) optionally other active ingredients, which do not substantially interfere with the stability of the co-formulation, (d) one or more non-polar organic solvent, (e) one or more polar organic co-solvent, (f) one or more non-ionic emulsifiers, (g) one or more anionic emulsifiers, and (h) optionally further formulation auxiliaries.



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Description

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Liquid herbicidal preparations

The invention pertains to the technical field of preparations (formulations) of specific crop protecting active ingredients (crop protection agents), more particularly to the field of co-formulations, i.e., the provision of two or more crop protecting active ingredients in one formulation. Specifically, the invention pertains to co-formulations of herbicidal active ingredients having different modes of action and types of activity, which are outstandingly suitable for controlling weed plants in crops of useful plants.

15 In many crops of useful plants, grasses are undesirable competitors which can be controlled only with considerable difficulty and at high costs. They germinate and grow in the soil over prolonged periods of time and can therefore only be effectively controlled with herbicides having foliar and soil action.

20 Examples of important weed grasses which occur in crops of useful plants all over the world and which are of high economic importance are:

Alopecurus myosuroides, Avena fatua and other forms of wild oats, Lolium spp., Phalaris spp., Setaria spp., Echinochloa spp., Poa spp., Bromus spp., Elymus repens, Sorghum spp. and others such as, for example, Agrostis, Panicum, etc.

25

Recently, some of these grasses have become difficult to control since, owing to the repeated application of herbicidal active compounds, resistant weed forms or forms which have a significantly reduced susceptibility towards these groups of active compounds have emerged. In this case, it is no longer possible to use the corresponding herbicides at application rates which ensure the desired herbicidal effect without causing considerable damage to the crops. Depending on the type of grass and herbicide, the resistance increase can vary considerably and can be so high that even amounts of 2 to 10 times the normal application rate are no longer sufficiently effective.

It is known from EP 0823995 that a combination of a herbicide from the 1,2,4-triazin-5-one type, specifically 6-alkyl-1,2,4-triazin-5-one type, such as metribuzin, and a herbicide from the type of (hetero)aryloxyphenoxy-propionates, such as fenoxaprop-P-ethyl, can be applied together to effectively control problem weeds, particularly also *Phalaris* spp. and *Lolium* spp.; detailed herbicidal compositions of the active ingredients (co-formulations) with specific formulation auxiliaries have not been disclosed by EP 0823995.

EP-A-0 614 608 describes synergistic herbicidal combinations for controlling slender foxtail which comprise certain combinations of (hetero)aryloxyphenoxypropionates and herbicides of other types of action, inter alia metribuzin. These described combinations are generally well suited for controlling grasses such as wild oats (*Avena fatua*) or slender foxtail (*Alopecurus myosuroides*) or weeds such as common chickweed (*Stellaria media*) in crops of cereals. Detailed herbicidal compositions of the active ingredients (co-formulations) with specific formulation auxiliaries have not been disclosed by EP-A-0614608.

It is known to use tank-mix combinations of metribuzin and clodinafop(-propargyl) for weed control in wheat crops; see Yadav Ashok et al. Environment & Ecology, Vol. 24S (3A), pp 853-856 (2006), MKK Publication, India.

The compounds of the group of the 1,2,4-triazin-5-ones including 6-alkyl-1,2,4-triazin-5-ones are known as selective systemic herbicides which act as inhibitors of photosynthesis (PS II inhibitor) and which are taken up predominantly via the roots, but also via the leaves. Hitherto, the herbicide metribuzin could be used in cereals and maize only at limited application rates; higher dosages, in particular on light soils and at high levels of precipitation, are not fully tolerated. On the other hand, metribuzin is an agent which is widely used in many countries in crops such as soybeans and potatoes. Higher dosages, as they are generally needed in cereals and maize for controlling grasses, are often not acceptable since these crops are not fully selective. Generally, the activity against many grasses is not satisfactory, so that in practice mixtures with other soil herbicides such as, for example, alachlor,

metolachlor or dimethenamide are used to control the grasses with better effectiveness.

Herbicides from the group of the (hetero)aryloxyphenoxy-propionic acids and
5 ketoenols are acetyl-CoA-carboxylase inhibitors and are particularly easily taken up
via the leaves. They are used by the post-emergence method for controlling grasses
in all important crops. Some of the important herbicides of these structural classes,
such as fenoxaprop-P-ethyl and clodinafop-propargyl or pinoxaden, respectively, can
also be used for controlling grasses in cereals. Compositions based on fenoxaprop-
10 P-ethyl, clodinafop-propargyl and/or pinoxaden are generally being used in
combination with safeners, i.e. herbicidal antidotes, for reducing the phytotoxicity on
crop plants.

It is thus desired to apply a combination of herbicides from the 6-alkyl-1,2,4-triazin-5-
15 one type and (hetero)aryloxyphenoxypropionic acid type or ketoenole type for
selective weed control, particularly those herbicidal combinations for selective weed
control in crops of useful plants, such as cereal crops.

The joint application of active ingredients has diverse technical aspects, of course,
20 depending on whether the active ingredients are to be combined only in a tank mix
or are to be actually provided in the form of a storable completed mixture.

Single active ingredients or active ingredient mixtures are generally employed not as
the active ingredients alone but instead, depending on the field of application and
desired physical application form, in combination with certain auxiliaries – that is,
25 they are “formulated”.

Active crop protecting ingredients can be formulated in a variety of ways, according
to the prevailing biological and/or physicochemical parameters. Formulation options
generally are: wettable powders (WP), oil-in-water or water-in-oil emulsions (EW or
30 EO), suspensions (SC), suspoemulsions (SE), emulsifiable concentrates (EC),
oil-dispersions (OD), granules for soil application or broadcast application, or water-
dispersible granules (WG). The stated types of formulation are known in principle

and are described for example in Winnacker-Küchler, "Chemische Technologie", volume 7, C.Hanser-Verlag, Munich, 4th edition 1986; van Valkenburg, "Pesticide Formulations", Marcel-Dekker N.Y., 1973; K.Martens, "Spray Drying Handbook", 3rd Ed., 1979, G.Goodwin Ltd. London.

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Tank-mixes of two different active ingredient formulations often cause problems through the incompatibility of formulation auxiliaries and incompatibility of an active ingredient with formulation auxiliaries of the other active ingredient formulation. Therefore, tank-mixes may not work well and are then not user-friendly.

10

Since the formulation type depends on the physicochemical properties of the active ingredients, the properties of the active ingredients are relevant for the choice of formulation auxiliaries such as solvent, emulsifiers, dispersants or wetting agents. The mixing of two different formulations thus can lead to incompatibilities of the components of a tank-mix with the consequence of coagulation, aggregation, crystallization, creaming or other separation processes which make it impossible to apply the tank-mix by spraying on the plants.

15

For ease of handling and for avoiding incompatibilities of different components a co-formulation is advantageous where the above-mentioned herbicides of different type and the formulation auxiliaries are present in fixed proportions, if a stable co-formulation can be prepared at all.

20

Commercial formulations of 6-alkyl-1,2,4-triazin-5-one herbicides such as metribuzin are usually aqueous suspension concentrates (SC), water-dispersible granules (WG) or wettable powders (WP).

25

Commercial formulations of (hetero)aryloxyphenoxypropionates such as fenoxaprop-P-ethyl or clodinafop-propargyl and their combinations with safeners are usually emulsifiable concentrates (EC) or oil-in-water emulsions (EW).

30

Commercial formulations of ketoenoles such as pinoxaden and their combinations with safeners such as cloquintocet-mexyl are usually emulsifiable concentrates (EC).

Due to the different types of formulations for the different active ingredients involved a stable co-formulation of said herbicides is thus a technical problem to be solved.

5 Among others, a specific problem is the tendency of metribuzin for crystallizing out from solutions in organic solvents.

Another specific problem is the tendency of fenoxaprop-P-ethyl and other (hetero)aryloxyphenoxypropionates for chemical instability in aqueous solvents.

10 The challenge is now to produce a chemically and physically stable formulation which allows the combined formulation of said herbicides of different type (co-formulation), wherein the co-formulation shall be storable in concentrated form and, optionally after dilution with water, is applicable under typical field conditions with a good biological efficacy.

15 It has now been found that surprisingly stable co-formulations of the type of emulsifiable concentrates (EC) of said herbicides can be prepared by combining the active ingredients with specific surfactant-solvent systems.

An object of the invention is a liquid herbicidal emulsifiable concentrate comprising

- 20 (a) the herbicidal active substance metribuzin,
(b) one or more herbicidal active substances selected from the group consisting of the ACCase inhibitors (b1), (b2) and (b3):
(b1) esters of fenoxaprop-P and esters of fenoxaprop,
(b2) esters of clodinafop,
25 (b3) pinoxaden,
(c) optionally other active ingredients, which do not substantially interfere with the stability of the co-formulation,
(d) one or more non-polar organic solvents,
(e) one or more polar organic co-solvents,
30 (f) one or more non-ionic emulsifiers,
(g) one or more anionic emulsifiers, and
(h) optionally further formulation auxiliaries.

Component (a) of the emulsifiable concentrates is the herbicidal active ingredient metribuzin (common name) (A1), having the chemical name 4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one, CAS RN [21087-64-9]. Metribuzin is generally known to be useful for pre- and post-emergence control of many grasses and broad-leaved weeds in soya beans, potatoes, tomatoes, sugar cane, alfalfa, asparagus, maize and cereals, at 0.07-1.45 kg/ha.

Component (b) of the emulsifiable concentrates is one or more herbicidal active ingredients selected from the group consisting of the herbicide groups (b1), (b2) and (b3) defined below:

(b1) Esters of fenoxaprop-P (common name) having the chemical name (R)-2-[4-[(6-chloro-2-benzoxazolyl)-oxy]-phenoxy]-propanoic acid, CAS RN [113158-40-0], preferably (C₁-C₄)alkylesters thereof, more preferably:
the active ingredient fenoxaprop-P-ethyl (common name) (B1.1), having the chemical name ethyl (R)-2-[4-[(6-chloro-2-benzoxazolyl)-oxy]-phenoxy]-propanoate, CAS RN [71283-80-2], a herbicide from the group of (hetero)aryloxyphenoxypropionates. Fenoxaprop-P-ethyl is generally known to be useful for post-emergence control of annual and perennial grass weeds in potatoes, beans, soya beans, beets, vegetables, peanuts, flax, oilseed rape, and cotton; and (when applied with the herbicide safener mefenpyr-diethyl) annual and perennial grass weeds and wild oats in wheat, rye, triticale and, depending on ratio, in some varieties of barley. Fenoxaprop-P-ethyl is an inhibitor of ACCase (Acetyl-CoA-carboxylase) in plants and thus inhibits fatty acid synthesis in plants.

Also included in this group are esters of fenoxaprop, preferably (C₁-C₄)alkylesters, more preferably the active ingredient fenoxaprop-ethyl (common name) (B1.2), having the chemical name ethyl 2-[4-[(6-chloro-2-benzoxazolyl)-oxy]-phenoxy]-propanoate, CAS RN [66441-23-4]. The racemate fenoxaprop-ethyl (B1.2) comprises the (R)-isomer fenoxaprop-P-ethyl (B1.1) together with its (S)-isomer in equal amounts;

- (b2) Esters of clodinafop (common name), having the chemical name (R)-2-[4-(5-chloro-3-fluoropyridin-2-yloxy)phenoxy]propionic acid, CAS RN [114420-56-3], preferably the alkyl, alkenyl or alkynyl esters thereof, having 1 to 12 carbon atoms in the alkyl moiety or 2 to 12 carbon atoms in the alkenyl or alkynyl moiety, respectively, more preferred the propargyl ester "clodinafop-propargyl" (common name) (B2.1), having the chemical name prop-2-ynyl (R)-2-[4-(5-chloro-3-fluoropyridin-2-yloxy)phenoxy]propionate, CAS RN [105512-06-9], a herbicide from the group of (hetero)aryloxyphenoxypropionates. Clodinafop-propargyl is generally known to be useful for post-emergence control of annual grasses, including Avena, Lolium, Setaria, Phalaris and Alopecurus spp., in cereals, at 30-60 g/ha, mainly in combination with the safener cloquintocet-mexyl. Clodinafop-propargyl is an inhibitor of ACCase (Acetyl-CoA-carboxylase) in plants and thus inhibits fatty acid synthesis in plants.
- (b3) Pinoxaden (common name) (B3.1), having the chemical name 8-(2,6-diethyl-p-tolyl)-1,2,4,5-tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropionate, CAS RN [243973-20-8]. Pinoxaden is a herbicide from the group of ketoenoles, more specifically of pyrazolidindiones, and is generally known to be useful for post-emergence control of annual grasses in wheat and barley at 30-60 g/ha in combination with the safener cloquintocet-mexyl. Pinoxaden is an inhibitor of ACCase (Acetyl-CoA-carboxylase) in plants and thus inhibits fatty acid synthesis in plants.

The co-formulations are usually preferred where metribuzin is combined with only one further herbicidal active ingredient of component (b).

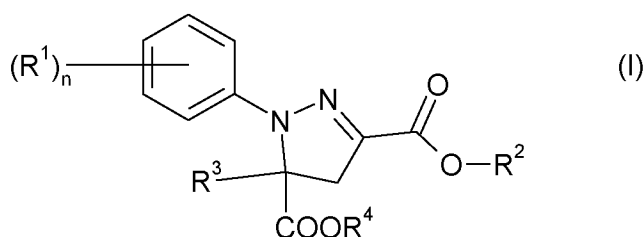
Herein, sometimes alpha-numeric abbreviations are used for the active ingredients. For instance, for metribuzin the abbreviation "(herbicidal) active ingredient (A1)", "component (A1)", "(chemical) compound (A1)", "herbicide (A1)" or simply "(A1)". Analogous abbreviations with different alphanumeric numbers are used for the other active ingredients of component (b), e. g. simply "(B1.1)" for fenoxaprop-P-ethyl, "(B1.2)" for fenoxaprop-ethyl,

"(B2.1)" for clodinafop-propargyl, and "(B3.1)" for pinoxaden; see also alphanumeric numbers used for safeners for component (c) further below.

In addition to components (a) and (b) the emulsifiable concentrates can optionally contain - as component (c) - further active ingredients for use in agriculture or plant protection such as safeners or active ingredients, such as e.g. other herbicides or fungicides, insecticides or acaricides, which do not substantially interfere with the stability of the co-formulation.

Preferred are as component (c) safeners selected from the group comprising (c1), (c2), (c3), (c4), and (c5) defined below:

(c1) 1-Phenyl-pyrazoline-3,5-dicarboxylic acid type safeners, such as those described in WO 91/07874, preferably safeners of the formula (I), or salts thereof,



in which

R¹ are identical or different and are halogen, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, nitro or (C₁-C₄)haloalkyl, preferably halogen, more preferably chloro,

n is an integer from 0 to 5, preferably from 0 to 3, more preferably 2,

R² is hydrogen or an unsubstituted or substituted aliphatic hydrocarbon radical having 1 to 18 carbon atoms,

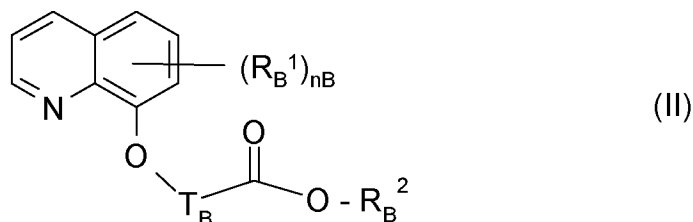
preferably is alkyl having a total of 1 to 18 carbon atoms, where the alkyl is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and (C₃-C₆)cycloalkyl,

more preferably is (C₁-C₆)alkyl, particularly methyl or ethyl,

R³ is hydrogen, (C₁-C₆)alkyl, (C₁-C₆)haloalkyl or (C₃-C₆)cycloalkyl,

more preferably is (C₁-C₄)alkyl, particularly methyl,
 R⁴ is hydrogen or an unsubstituted or substituted aliphatic hydrocarbon
 radical having 1 to 18 carbon atoms,
 preferably is hydrogen or alkyl having a total of 1 to 18 carbon atoms,
 where the alkyl is unsubstituted or substituted by one or more radicals
 selected from the group consisting of halogen, (C₁-C₄)alkoxy,
 (C₁-C₄)alkylthio and (C₃-C₆)cycloalkyl,
 more preferably is hydrogen or (C₁-C₆)alkyl, particularly methyl or ethyl,
 wherein a preferred safener is the compound having the chemical name
 ethyl (2,4-dichlorophenyl)-5-(ethoxycarbonyl)-5-methyl-2-
 pyrazoline-3-carboxylate (C1.1) ["Mefenpyr-diethyl" (common name)], see
 "The Pesticide Manual", 15th edition 2009, British Crop Protection Council;

(c2) (Quinoline-8-yloxy)-alkylcarboxylic acid type safeners as described in
 EP-A-86750, EP-A-94349, EP-A-191736, EP-A-0492366 or WO 2002/34048,
 preferably safeners of the formula (II),



in which

R_B¹ is halogen, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, nitro or (C₁-C₄)haloalkyl,
 preferably halogen, more preferably chloro;
 n_B is an integer of from 0 to 5, preferably 0 to 3, particularly 1;
 R_B² hydrogen or an unsubstituted or substituted aliphatic hydrocarbon
 radical having 1 to 18 carbon atoms,
 preferably is hydrogen or alkyl, alkenyl or alkynyl having in each case a
 total of 1 to 18 carbon atoms or is alkyl having a total of 1 to 10 carbon
 atoms, where the alkyl is substituted by one to three halogen atoms or
 by one (C₁-C₄)alkoxy, (C₂-C₄)alkenyloxy, (C₂-C₄)alkynyloxy or
 (C₃-C₆)cycloalkyl;

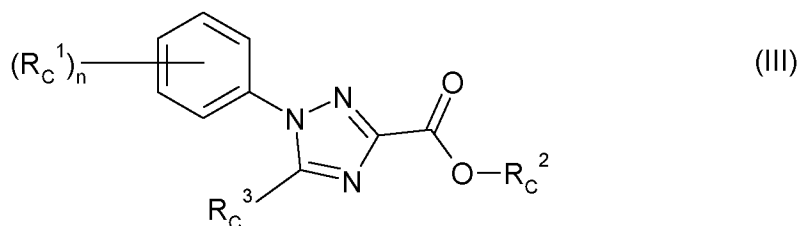
more preferably is hydrogen or (C₁-C₁₀)alkyl, particularly methyl, ethyl, n- or i-propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl (each term including all isomers),

more preferably is 2-heptyl (= 1-methyl-hexyl = mexyl);

5 T_B is alkandiyl selected from -CH₂- or -CH(CH₃)-, preferably methylene, wherein a preferred safener is:

- 1-methylhexyl (5-chloro-8-chinolinoxyl)acetate (C2.1) ["cloquintocet-mexyl"(common name)], see "The Pesticide Manual", 15th edition 2009, British Crop Protection Council;
- 10 - 1,3-dimethyl-but-1-yl (5-chloro-8-chinolinoxyl)acetate (C2.2),
- 4-allyloxy-butyl (5-chloro-8-chinolinoxyl)acetate (C2.3),
- 1-allyloxy-prop-2-yl (5-chloro-8-chinolinoxyl)acetate (C2.4),
- ethyl (5-chloro-8-chinolinoxyl)acetate (C2.5),
- methyl (5-chloro-8-chinolinoxyl)acetate (C2.6),
- 15 - allyl (5-chloro-8-chinolinoxyl)acetate (C2.7) or
- 2-(2-propyliden-iminoxy)-1-ethyl (5-chloro-8-chinolinoxyl)acetate (C2.8),
- 2-oxo-prop-1-yl (5-chloro-8-chinolinoxyl)acetate (C2.9)

20 (c3) 1-Phenyl-1,2,4-triazole-3-carboxylic acid type safeners as described in EP-A-174562 and EP-A-346620, for example compounds of the formula (III) or salts thereof:



in which

- 25 R_C¹ are identical or different and are halogen, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, nitro or (C₁-C₄)haloalkyl, preferably halogen, more preferably chloro,
- n is an integer from 0 to 5, preferably from 0 to 3, more preferably 2,
- R_C² is hydrogen or an unsubstituted or substituted aliphatic hydrocarbon radical having 1 to 18 carbon atoms,

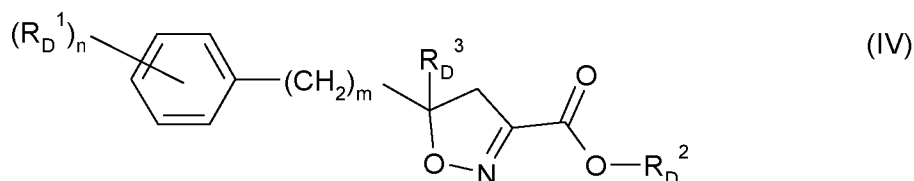
preferably is alkyl having a total of 1 to 18 carbon atoms, where the alkyl is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and (C₃-C₆)cycloalkyl,

5 more preferably is (C₁-C₆)alkyl, particularly methyl or ethyl,

R_C³ is hydrogen, (C₁-C₆)alkyl, (C₁-C₆)haloalkyl or (C₃-C₆)cycloalkyl, more preferably is (C₁-C₄)haloalkyl, particularly trichloromethyl,

wherein a preferred safener is the compound having the chemical name
10 1-(2,4-dichlorophenyl)-5-trichloromethyl-(1H)-1,2,4-triazole-3-carboxylate (C3.1) ["fenchlorazole-ethyl" (common name)];

(c4) Isoxazoline-carboxylic acid type safener as described in WO 91/08202 and WO 95/07897, preferably the compounds of the formula (IV) or salts thereof



in which

R_D¹ are identical or different and are halogen, (C₁-C₄)alkyl, (C₁-C₄)alkoxy, nitro or (C₁-C₄)haloalkyl, preferably halogen, more preferably chloro,

20 n is an integer from 0 to 5, preferably from 0 to 3, more preferably zero,

R_D² is hydrogen or an unsubstituted or substituted aliphatic hydrocarbon radical having 1 to 18 carbon atoms,

preferably is alkyl having a total of 1 to 18 carbon atoms, where the alkyl is unsubstituted or substituted by one or more radicals selected from the group consisting of halogen, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and (C₃-C₆)cycloalkyl,

25

more preferably is (C₁-C₆)alkyl, particularly methyl or ethyl,

R_D³ is hydrogen, (C₁-C₆)alkyl, (C₁-C₆)haloalkyl, (C₃-C₆)cycloalkyl or substituted or unsubstituted phenyl, preferably unsubstituted phenyl or

phenyl substituted by one or more selected from the group consisting of halogen, (C₁-C₄)alkyl, (C₁-C₄)alkoxy and (C₁-C₄)haloalkyl, particularly unsubstituted phenyl,

m is 0 or 1, preferably zero,

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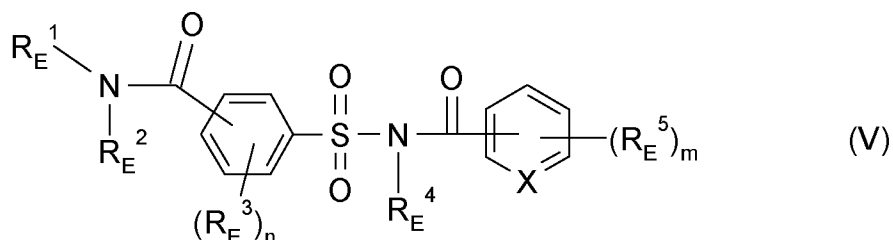
preferably safener compounds:

- ethyl 5,5-diphenyl-2-isoxazoline-3-carboxylate (C4.1) ["isoxadifen-ethyl" (common name)],
- propyl 5,5-diphenyl-2-isoxazoline-3-carboxylate (C4.2),
- 10 - ethyl 5-phenyl-2-isoxazoline-3-carboxylate (C4.3),
- ethyl 5-(4-fluorophenyl)-5-phenyl-2-isoxazoline-3-carboxylate (C4.4)
- ethyl 5-(2,4-dichlorobenzyl)-2-isoxazoline-3-carboxylate (C4.5),

(c5) acylsulfamoylbenzamide type safener as described in WO-A-99/16744,

15

preferably compounds of the formula (V) or salts thereof,



in which

X is CH or N, preferably CH,

20

R_E¹ is hydrogen, aliphatic heterocyclyl having 3 to 6 ring atoms and 1 to 3 heteroatoms selected from N, O and S or is a hydrocarbon radical having 1 to 12 carbon atoms, where the two last-mentioned radicals are unsubstituted or substituted by one or more identical or different radicals selected from the group consisting of halogen, cyano, nitro, (C₁-C₄)alkoxy, (C₁-C₄)alkylthio and in case of cyclic basic groups also (C₁-C₄)alkyl and (C₁-C₄)haloalkyl, preferably (C₁-C₆)alkyl or (C₃-C₆)cycloalkyl, more preferably methyl, ethyl or cyclopropyl,

25

- R_E^2 is hydrogen, (C₁-C₆)alkyl or (C₃-C₆)cycloalkyl, more preferably hydrogen, methyl or ethyl, particularly hydrogen,
 R_E^3 are identical or different where each is halogen, cyano, nitro, (C₁-C₄)alkyl, (C₁-C₄)haloalkyl, (C₁-C₄)alkoxy, (C₁-C₄)haloalkoxy or (C₁-C₄)alkylthio, preferably halogen or methyl,
 R_E^4 is hydrogen or (C₁-C₄)alkyl, preferably hydrogen,
 R_E^5 are identical or different and each is halogen, cyano, nitro, (C₁-C₄)alkyl, (C₁-C₄)haloalkyl, (C₁-C₄)alkoxy, (C₁-C₄)haloalkoxy and (C₁-C₄)alkylthio, preferably halogen, (C₁-C₄)alkyl or (C₁-C₄)alkoxy, particularly 2-methoxy,
n is an integer from 0 to 4, preferably zero and
m is, in the case that X is CH, an integer from 0 to 5, preferably 0, 1 or 2, and, in the case that X is N, an integer from 0 to 4, preferably 0 or 1,

preferably the safener compound:

4-(2-methoxybenzoylsulfamoyl)-N-cyclopropylbenzamide (C5.1)
["cyprosulfamide" (common name)]

Most preferred is the combination of (A1) metribuzin and (B1.1) fenoxaprop-P-ethyl, optionally in the presence of safener and preferably in the presence of the safener mefenpyr-diethyl (C1.1) or cloquintocet-mexyl (C2.1), more preferably in the presence of mefenpyr-diethyl (C1.1).

Also preferred is the combination of (A1) metribuzin and (B2.1) clodinafop-propargyl, optionally in the presence of safener and preferably in the presence of the safener cloquintocet-mexyl (C2.1) or mefenpyr-diethyl (C1.1), more preferably in the presence of cloquintocet-mexyl (C2.1).

Also preferred is the combination of (A1) metribuzin and (B3.1) pinoxaden optionally in the presence of safener and preferably in the presence of the safener cloquintocet-mexyl (C2.1) or mefenpyr-diethyl (C1.1).

The specific active ingredients and their common names are known, see The Pesticide Manual, 15th. Edition, British Crop Protection Council, 2009.

In addition to the active ingredients of components (a) and (b) and optional components (c), the co-formulations according to the invention comprise a non-polar organic solvent as component (d).

5

Examples of suitable solvents (d) are comprising:

- aliphatic and/or aromatic hydrocarbons, such as
 - mineral oils, paraffins,
 - toluene, xylenes,
 - 10 - naphthalene derivatives, more particularly 1-methylnaphthalene, 2-methylnaphthalene,
 - mixtures of aromatic compounds having 6 to 16 C-atoms, such as the Solvesso® series (ESSO) with the products Solvesso® 100 (b.p. 164-180°C), Solvesso® 150 (b.p. 181-207°C), and Solvesso® 200 (b.p. 219-282°C), Solvesso® 150 ND (b.p. 179-194°C), Solvesso® 200 ND (initial b.p. 242°C), or
 - 15 aromatic solvents from the Caromax™ series (Petrochem carless) such as Caromax™ 20, 26, 28 and Caromax™ LN 20, LN 26, LN 28,
 - aliphatics having 6 to 20 carbon atoms and mixtures thereof, which
 - 20 may be linear or cyclic, such as the products of the Shellsol® series, types T and K, or BP-n paraffins,
 - halogenated aliphatic hydrocarbons such as methylene chloride,
 - halogenated aromatic hydrocarbons such as chlorobenzene, chloro-toluenes or chloro-xylenes,
 - 25 and mixtures thereof.

Preferred solvents (d) have very low solubilities in water and a high capability of dissolving a wide range of active ingredients. Preferred solvents (d) are, for instance, aliphatic and/or aromatic hydrocarbons and/or mixtures thereof, such as mineral oils

30 with high aromatic content or mixtures of aromatics.

In addition to the components (a) and (b), optional components (c), and solvent (d) the co-formulations according to the invention comprise a polar organic co-solvent as component (e). Examples of suitable co-solvents (e) include

- 5 (e1) lipophilic alcohols, preferably lipophilic aliphatic or cycloaliphatic alcohols, more preferably lipophilic monohydric alcohols having 3 to 16 carbon atoms in the aliphatic or cycloaliphatic moiety, for instance (C₃-C₁₄)alkanols, such as n-propanol, isopropanol, n-, iso-, sec- t-butanol, pentanols and (C₆-C₁₂)alkanols, preferably (C₄-C₁₂)alkanols, such as isobutanol or (C₆-C₁₂)alkanols, more preferably (C₆-C₁₂)alkanols, such as n-hexanol, i-hexanol, n-heptanol, i-heptanol, n-octanol, 2-ethylhexanol, n-decanol and n-dodecanol, 10 or cycloalkanols such as cyclohexanol, or cycloalkyl-alkanols such as tetrahydrofurfuryl alcohol, or lipophilic aliphatic diols such as 2-methyl-2,4-pentanediol, or, also preferably, lipophilic alcohols based on alkanols substituted with aromatic groups, such as benzylalcohol or phenylethanol, preferably benzylalcohol, 15
- (e2) esters such as triacetin (acetic triglyceride), butyrolactone, propylene carbonate, triethyl citrate, lactic (C₁-C₁₀)alkylesters and (C₁-C₂₂)alkyl phthalates, especially (C₄-C₈)alkyl phthalates,
- 20 (e3) ethers, such as diethyl ether, tetrahydrofuran (THF), dioxane, alkylene glycol monoalkyl and dialkyl ethers such as, for example, propylene glycol monomethyl ether, especially Dowanol® PM (propylene glycol monomethyl ether), propylene glycol monoethyl ether, ethylene glycol monomethyl ether or ethylene glycol monoethyl ether, diglyme and tetraglyme,
- 25 (e4) N,N-dialkylated carboxylic acid amides having 1 to 18 carbon atoms in the carboxylic acid moiety, preferably N,N-dialkylated alkanolic amides such as dimethylformamide (DMF), dimethylacetamide, dimethylcaprylyl/capric fatty acid amide, N,N-dimethyloctanamide, N,N-dimethyldecanamide, N,N-dimethyldodecanamide,
- 30 (e5) cyclic amides such as N-alkylpyrrolidones, e. g. N-methylpyrrolidone or N-octylpyrrolidone,

- (e6) ketones such as the water-soluble acetone, but also water-immiscible ketones such as cyclohexanone or isophorone,
- (e7) nitriles such as acetonitrile, propionitrile, butyronitrile, and benzonitrile,
- (e8) phosphates such as tris-((C₁-C₁₀)alkylphosphates,
- 5 (e9) sulfoxides and sulfones such as dimethyl sulfoxide (DMSO) and sulfolane,
- (e10) oils in general, examples being natural, semisynthetic and synthetic oils, preferably vegetable-based oils such as corn germ oil, soy bean oil or rapeseed oil, rapeseed oil alkyl esters, especially rapeseed oil methyl ester, and mixtures thereof.
- 10 Preferred as component (e) are polar aprotic co-solvents selected from lipophilic alcohols, esters, N,N-dialkylated carboxylic acid amides having 1-18 carbon atoms in the carboxylic acid moiety, cyclic amides, ketones and mixtures of the aforementioned co-solvents.
- More preferred as component (e) are polar aprotic co-solvents, particularly selected
- 15 from carboxylic acid amides having 6 to 12 carbon atoms in the acyl moiety, such as dimethylcaprylyl/capric fatty acid amide, N,N-dimethyloctanamide, N,N-dimethyldecanamide, N,N-dimethyldodecanamide and mixtures thereof.
- Commercially available are solvents comprising mixtures of N,N®-
- dimethyloctanamide and N,N-dimethyldecanamide, such as Hallcomid™ M-8-10
- 20 (Stepan Co.), Genagen® 4166 (Clariant), Agnique® KE 3658 (Cognis/BASF) and Armid® DM 810 (Akzo Nobel).

The co-formulations according to the invention comprise one or more non-ionic emulsifiers as component (f). Examples of suitable non-ionic emulsifiers (f) are

25 selected from the groups (f1) and (f2):

- (f1) Aromatic-based non-ionic surfactants, for example, phenols substituted by one or more alkyl groups and subsequently derivatized, which are soluble in the organic solvent phase and which emulsify this phase – together with the active
- 30 ingredients dissolved therein – on dilution with water (to form the spray liquor).

A typical derivatization is alkoxylation by reacting the phenols with epoxides resulting in poly(alkyleneoxy) phenyl ethers. With regard to alkoxylation, in the section for non-ionic, but also in the sections for anionic and other surfactants (further below) having been alkoxyated, the stated type and degree or polyalkoxylation is specified by the alkyleneoxy units and their number per polyalkyleneoxy moiety or moieties; examples for alkyleneoxy units are 1,2-ethyleneoxy (EO-unit or just "EO"), 1,2-propyleneoxy (PO-unit or just "PO"), 1,2-butylenoxy, 2,3-butylenoxy-, and 2,2-dimethyl-1,2-ethyleneoxy ("BO" units if not further specified); if not further specified 1,2-ethyleneoxy units are preferred as alkyleneoxy units.

Examples of surfactants of the (f1) type are as follows:

(f1.1) phenyl (C₁-C₄)alkyl ethers or (poly)alkoxylated phenols [= phenol (poly)alkylene glycol ethers], for example with 1 to 50 alkyleneoxy units in the (poly)alkyleneoxy moiety, the alkylene moiety having preferably 1 to 4 carbon atoms in each case, preferably phenol reacted with 3 to 10 mol of alkylene oxide, for example ethoxylated phenol having 4 to 10 EO, available commercially in the form of the Agrisol® products (Akcros);

(f1.2) (poly)alkylphenols or (poly)alkylphenol alkoxyates [= polyalkylphenol (poly)alkylene glycol ethers], for example with 1 to 12 carbon atoms per alkyl radical and 1 to 150 alkyleneoxy units in the polyalkyleneoxy moiety, preferably ethoxylated tri-n-butylphenol, triisobutylphenol or tri(sec-butyl)phenol having 1 to 50 ethyleneoxy (EO-) units in the polyalkyleneoxy moiety, for example

ethoxylated nonylphenol with 4 to 50 EO, available commercially in the form of the Arkopal® products (Clariant);

ethoxylated triisobutylphenol or tri(sec-butyl)phenol having 4 to 50 EO, available commercially in the form of the Sapogenat® T products (Clariant), for example, e.g. Sapogenat® T060 [ethoxylated tri(sec-butyl)phenol with 6 EO] or T080 [with 8 EO] or T300 [with 30 EO];

(f1.3) poly(arylalkyl)-phenols or poly(arylalkyl)-phenol alkoxyates [= poly(arylalkyl)-phenol (poly)alkylene glycol ethers], for example tristyrylphenol polyalkylene

glycol ethers having 1 to 150 alkyleneoxy units in the polyalkyleneoxy moiety, such as

ethoxylated tristyrylphenol having 1 to 150 ethyleneoxy units in the polyalkyleneoxy moiety, for example Emulsogen® TS products (Clariant), e.g.

5 ethoxylated tristyrylphenol with 10 EO (Emulsogen® TS 100), with 16 EO (Emulsogen® TS 160), with 20 EO (Emulsogen® TS 200), with 29 EO (Emulsogen® TS 290), with 40 EO (Emulsogen® TS 400), with 54 EO (Emulsogen® TS 540) and with 60 EO (Emulsogen® TS 600)

or ethoxylated tristyrylphenols of Rhodia such as, for example,
10 Soprophor CY/8®, Soprophor BSU®, Soprophor® S and TS products;;

alkoxylated tristyrylphenol with PO- and EO-units, for example, with 4 PO and 20 EO (Soprophor® 796 P, Rhodia);

(f2) Non-aromatic non-ionic surfactants, which are emulsifiers like the aromatic
15 surfactants (f1) but may differ in parameters such as HLB index, solubility or solvent or emulsifier power concerning the organic phase or the active ingredients.

Examples for such surfactants or emulsifiers are:

(f2.1) Fatty alcohol alkoxylates having 10 to 24 carbon atoms with 0 to 60 EO and/or
20 0 to 20 PO and/or 0 to 15 BO in any order, and/or where the terminal hydroxyl groups of these compounds are end group-capped by an alkyl, cycloalkyl or acyl radical having 1 to 24 carbon atoms. Examples of such compounds are as follows:

Genapol® C, LA, O, OA, OX, T, UD, X and XM products from Clariant, such
25 as iso-tridecylalcohol polyglykolether with 3 EO (Genapol® X 030), with 5 EO (Genapol® X 050), with 6 EO (Genapol® X 060), with 8 EO (Genapol® X 080), with 9 EO (Genapol® X 090), with 10 EO (Genapol® X 100), with 15 EO (Genapol® X 150), Plurafac® and Lutensol®A, AT, ON, and TO products from BASF, Agnique® FOH products from Cognis, Ethylan® products from Akzo-Nobel, Empilan® products from Huntsman;

30 (f2.2) Fatty acid alkoxylates and triglyceride alkoxylates such as the Emulsogen® EL products from Clariant, e.g. ethoxylated castor oil such as with 20 EO (Emulsogen® EL 200), with 30 EO (Emulsogen® EL 300), with 36 EO

(Emulsogen® EL 360), with 40 EO (Emulsogen® EL 400), with 540 EO (Emulsogen® EL 540), the Agnique® CSO products of Cognis, e.g. Agnique CSO-40, Termul® 1283, 1284, 1285, 2507, 3512 or 3540 of Huntsman or the Alkamuls® OR products from Rhodia, e.g. Alkamus® OR/40;

- 5 (f2.3) Fatty acid amide alkoxylates such as the Comperlan® products from Cognis or the Amam® products from Rhodia;
- (f2.4) Fatty amine alkoxylates such as the Agnique CAM, SAM or TAM ® products from Cognis or the Genamin® C, S, O or T products from Clariant;
- 10 (f2.5) Alkylene oxide adducts of alkandiols such as the Surfynol® products from Air Products;
- (f2.6) Sugar derivatives such as amino sugars and amido sugars from Clariant, glucitols from Clariant, alkylpolyglycosides in the form of the Agnique® PG products from Cognis; sorbitan esters in the form of the Span® or Tween® products from Croda or Agnique® S from Cognis; or cyclodextrin esters or
- 15 ethers from Wacker;
- (f2.7) Surface-active cellulose derivatives and algin, pectin, and guar derivatives such as the Tylose® products from ShinEtzu, the Manutex® products from Kelco, and guar derivatives from Cesalpina;
- (f2.8) Alkylene oxide adducts on a polyol basis, such as Polyglykol® products from
- 20 Clariant; Interface-active polyglycerides and their derivatives from Clariant or Pluriol® E and P products from BASF;
- (f2.9) Surface-active compounds on a silicone or silane basis, such as the Tegopren® products from Evonik and the SE® products from Wacker, and also the Bevaloid®, Rhodorsil® and Silcolapse® products from Rhodia
- 25 (f2.10) Copolymers consisting of EO, PO and/or BO units, such as, for example, block copolymers such as the Pluronic® products from BASF and the Synperonic® products from Croda with a molecular weight of 400 to 10⁸, Genapol® PF products from Clariant;
- (f2.11) Alkylene oxide adducts of C₁-C₉ alcohols such as Atlox® 5000 from Croda or
- 30 Emulsogen® 3510 from Clariant;
- (f2.12) Surfactant-type polyvinyl compounds such as modified PVP, such as the Luviskol® products from BASF and the Agrimer® products from ISP, or the

derivatized polyvinyl acetates, such as the Mowilith® products from Celanese, or the polyvinyl butyrates, such as the Lutonal® products from BASF, the Vinnapas® and the Pioloform® products from Wacker, or modified polyvinyl alcohols such as the Mowiol® products from Kuraray,

- 5 (f2.13) Surface-active polymers based on maleic anhydride and/or reaction products of maleic anhydride, and also copolymers comprising maleic anhydride and/or reaction products of maleic anhydride, such as the Agrimer® VEMA products from ISP.

- 10 Preferred non-ionic emulsifiers (f) are:

(poly)alkylphenols or (poly)alkylphenol alkoxyates, poly(arylalkyl)-phenols, poly(arylalkyl)-phenol alkoxyates, fatty alcohol alkoxyates, fatty acid alkoxyates, triglyceride alkoxyates, sorbitan esters, copolymers consisting of EO, PO and/or BO units and alkylene oxide adducts of C₁-C₉ alcohols.

15

More preferred non-ionic emulsifiers (f) are:

emulsifiers from the group (f1.3), preferably alkoxyated tristyrylphenol with PO- and EO-units, such as Soprophor® 796 P (Rhodia) having 4 PO and 20 EO or Sophrophor® TSP 461;

20

emulsifiers from the group (f2.1), preferably alkoxyated fatty alcohols with EO-units, more preferably iso-tridecylalcohol polyglycolether with 3-15 EO such as Genapol® X 060 (Clariant) or Empilan® KI6 (Huntsman);

emulsifiers from the group (f2.2), preferably ethoxylated castor oils such as Emulsogen® EL 400, Agnique® CSO-40, Termul® 3540 or Alkamus® OR/40, all
25 having 40 EO.

The co-formulations according to the invention comprise one or more anionic emulsifiers as component (g). Examples of suitable anionic emulsifiers (g) are selected from the groups (g1) and (g2):

30

(g1) Aromatic-based anionic surfactants which are emulsifiers, for example,

(g1.1) compounds which formally represent the reaction product of the non-ionic emulsifiers described under (f1.1) to (f1.3) with sulfuric acid or phosphoric acid, and their inorganic salts (e.g., alkali metal, alkaline earth metal or ammonium salts) and organic salts (e.g., amine- or alkanolamine-based salts),

examples thereof are:

phenol ethoxylate, phosphated, in the form of the free acid, such as Phospholan® PHB14 from Akzo; (poly)alkylphenol ethoxylate, phosphated, such as Rhodafac® PA and PS products from Rhodia; ethoxylated poly(arylalkyl)-phenol ethoxylate, phosphated, such as Agnique® PE products from Cognis, Empiphos® (Huntsman) or Soprophor® products from Rhodia; ethoxylated poly(arylalkyl)phenol ethoxylate phosphate ester neutralized with bases (salt-form) for example Dispersogen® TP products from Clariant, Agnique® PE products from Cognis or Soprophor® FLK (Rhodia);

(g1.2) (poly)alkyl- and poly(arylalkyl)-benzenesulfonates neutralized with suitable bases, for example having 1 to 12 carbon atoms per alkyl radical and having up to 3 styrene units in the poly(arylalkyl) radical, preferably (linear) dodecylbenzenesulfonic acid and the oil-soluble salts thereof, such as the isopropylammonium salt of dodecylbenzenesulfonic acid, for example:

iso-C₁₂-alkyl-benzenesulfonate calcium salt such as Phenylsulfonate™ CA (Clariant), Calsogen® AR 100 or AR 100 ND or EH (Clariant), varying in additional solvent component such as mineral oils or (C₄-C₈)alkanols, branched dodecylbenzolsulfonate calcium salt such as Emcol® P 1860 (Akzo),

n-C₁₂-alkyl-benzenesulfonate calcium salt such as Phenylsulfonate CAL, Calsogen® 100 or ARL 100 ND or ARL 48 or 4814 (Clariant), Rhodacal® 60 BE (Rhodia), varying in additional solvent component,

(g1.3) acidic (poly)alkyl- and poly(arylalkyl)-benzenesulfonates for example having 1 to 12 carbon atoms per alkyl radical and having up to 3 styrene units in the poly(arylalkyl) radical, for example, acidic (linear) dodecylbenzenesulfonate, available commercially in the form of the Marlon® products (Sasol);

(g2) Non-aromatic anionic surfactants, which are emulsifiers like the aromatic surfactants (g1) but may differ in parameters such as HLB index, solubility or solvent or emulsifier power concerning the organic phase or the active ingredients.

5 Examples for such surfactants or emulsifiers are:

(g2.1) Anionic derivatives of the products described under (f2.1) and (f2.2), in the form of 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
10 Genapol®LRO, Sandopan® products, Hostaphat/Hordaphos® products from Clariant, Servoxyl® products from Elementis, Agnique® SLS products (Cognis);

(g2.2) salts of aliphatic, cycloaliphatic, and olefinic carboxylic acids and polycarboxylic acids, and also alpha-sulfo fatty acid esters as obtainable from
15 Cognis,

(g2.3) Sulfosuccinates, alkanesulfonates, paraffinsulfonates and olefinsulfonates and their inorganic (e.g., alkali metal and alkaline earth metal) and 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
20 Dow, Empimin® products from Huntsman, Marlon®-PS65 from Condea,

(g2.4) Sulfosuccinamates such as the Aerosol® products from Cytec or the Empimin® products from Huntsman,

(g2.5) Surface-active polyacrylic and polymethacrylic derivatives such as the Sokalan® products from BASF.

25 Preferred anionic emulsifiers (g) are:

phosphated or sulfated (poly)alkylphenol alkoxylates, phosphated or sulfated poly(arylalkyl)-phenol alkoxylates, (poly)alkyl- and poly(arylalkyl)-benzenesulfonates in acidic or salt form and sulfosuccinates.

30 More preferred anionic emulsifiers (g) are:

emulsifiers from the group (g1.2), preferably emulsifiers based on calcium salt of dodecylbenzenesulfonic acid, such as Rhodacal® 60 BE (Rhodia) or Calsogen® 4814 (Clariant), Atlox® 4838B X-MSU (Croda), Ninate® 60E X-MSU (Stepan) or Nansa® EVM 70/2E (Huntsman).

5

The co-formulations according to the invention may comprise - as component (h) - one or more additional formulation auxiliaries of other type, such as further solvents, further surfactants, agents which influence the thixotropy and rheology of the emulsifiable concentrates (e. g. thickeners), frost preventatives, evaporation
10 inhibitors, preservatives, odorants, colorants, defoamers, fillers, carriers, and dyes, pH modifiers (buffers, acids, and bases), and others.

For example, the formulations of the invention may comprise further solvents, without losing the advantageous properties of the surfactant-solvent system. In
15 connection with the present invention, examples of suitable additional solvents include apolar solvents, small amounts of polar protic solvents, aprotic dipolar solvents, and mixtures thereof.

Examples for polar protic solvents which may be present in small amounts (preferably less than 10 percent by weight, more preferably less than 5 percent by
20 weight of the formulation) comprise hydrophilic alkanols such as e. g. methanol or ethanol.

Additionally, the formulations usually contain some amount of water, due to the content of water which is often a minor component in the surfactants employed (preferably less than 5 percent by weight, more preferably less than 3 percent by
25 weight, particularly less than 1 percent by weight of the formulation).

Additionally, the formulations may contain minor amounts of components which are introduced by way of the surfactants employed and which have some function, for instance to dissolve the surfactants or to modify the rheology of the surfactants, such
30 as solvents, salts or carriers. Unless these components are not already part of the components (d) to (g) mentioned above the amount of such components (h) in the preparation is preferably less than 10 percent by weight, more preferably less than 5

percent by weight, more preferably less than 3 percent by weight, particularly less than 1 percent by weight of the formulation.

In addition, the formulations of the invention may comprise further surface active agents, without losing the advantageous properties of the surfactant-solvent system. Examples of such surface active agents are:

- Alkylene oxide adducts of fatty amines, quaternary ammonium compounds having 8 to 22 carbon atoms (C₈–C₂₂), such as, for example, the Dodigen® products from Clariant;
- Surface-active zwitterionic compounds such as taurides, betaines, and sulfobetaines, in the form of Tegotain® products from Goldschmidt, Hostapon®T and Arkopon®T products from Clariant;
- Surface-active polyamides such as modified gelatins or derivatized polyaspartic acid from Bayer, and derivatives thereof.

Examples of optional further formulating auxiliaries (h) include frost preventatives and evaporation inhibitors such as glycerol, for example, in an amount of 2 to 10% by weight, or preservatives, e.g., Mergal K9N® (Riedel) or Cobate C®, for example, in the customary use concentrations for the particular agents employed in each case.

The greater the number of structurally different active ingredients to be combined in a formulation, the greater the restrictions on formulation freedom that apply. Alternatively, a storable emulsifiable concentrate generally offers the advantage over a tank mix that the active ingredients and formulating auxiliaries are present in proportions tailored to one another, whereas with a tank mix the proportions must be set by the user each time and, depending on the formulations used for the individual components, there may be incompatibilities among the auxiliaries.

In addition to the purely formulation-related object of providing a stable concentrated EC-formulation which when diluted with water produces spray liquors (emulsions) having properties that are advantageous from a physical/applications standpoint, a

preferred additional object is that of providing formulations having biologically advantageous properties.

5 The auxiliaries to be used for the formulations ought to have broad suitability for use and ought to support, and as far as possible not adversely affect, the biological properties of the active ingredients used.

10 With the surfactant/solvent systems of the invention comprising the components (b) and (c) that are used it is now possible, surprisingly, to produce stable emulsifiable concentrates for metribuzin combined with the ACCase inhibitors Fenoxaprop(-P)-ethyl, Clodinafop-propargyl and/or Pinoxaden, optionally in the presence of safeners as components (c). Furthermore, the surfactant system of the invention favorably influences the herbicidal activity of the active ingredients incorporated and providing a favorable crop-safety in cereals, especially when a safener is contained as
15 component (c).

The surfactant/solvent system of components (d) to (g) of the invention allows the production of emulsifiable concentrates with additional active ingredients (c), other than those already mentioned above for (a) to (c), provided that they exhibit similar
20 properties in terms of their solubilities and stabilities. As additional herbicides are possible, for example, herbicides from the group of the phenoxyphenoxypropionates such as diclofop-methyl, cyhalofop-butyl, the heteroaryloxyphenoxypropionates such as fluazifop-butyl, fluazifop-P-butyl, haloxyfop-methyl, haloxyfop-etotyl, haloxyfop-P-methyl, propaquizafop, quizalofop-ethyl, quizalofop-P-ethyl, herbicides from the
25 group of the triazinones such as met amitron, other herbicides such as benfuresate, or other active ingredients such as the fungicide prochloraz and/or insecticides such as deltamethrin, or other safeners.

This shows the flexibility of the surfactant/solvent system described. The compounds stated are known to the skilled worker from "The Pesticide Manual", British Crop
30 Protection Council, 15th edition, 2009.

On dilution with water, the emulsifiable concentrates produce water-in-oil or oil-in-water emulsions, with corresponding selection of the individual components.

Depending on composition, therefore, EC-formulations are obtainable that can be diluted either with water or with oil, with retention of the colloidal structure.

- 5 Accordingly, the ready-to-use spray-liquors obtainable from the above-described EC-formulations via dilution are additionally provided by the invention.

The weight ratios of the combined active herbicidal ingredients of type (a) and (b) and, optionally, (c) may vary within wide limits, but generally are in the following
10 ranges by weight:

The ratio (a):(b) is for examples of from (10):(1) to (1):(5), preferably (5):(1) to (1):(1), more preferably (3):(1) to (1):(1), particularly (2):(1) to (1.5):(1).

The ratio (b):(c) is for examples of from (10):(1) to (1):(1), preferably (6):(1) to (1):(1), more preferably (5):(1) to (2):(1), particularly (5):(1) to (3):(1), preferably for safener
15 mefenpyr-diethyl as component (c).

The ratio (a):(b):(c) for examples from (15):(5):(1) to (5):(1):(1), preferably from (10):(5):(1) to (5):(2):(1), preferably for mefenpyr-diethyl as component (c).

The application rates of the herbicide active ingredients may vary within a wide
20 range and are situated generally in the range of 20 and 500 g of active substance per hectare (= g a.i./ha) for component (a), preferably between 50 and 300 g a.i./ha, more preferably 100 and 250 g a.i./ha, particularly from 120 to 230 g a.i./ha.

The application rate of the herbicide (b) may vary within a wide range and is situated generally in the range of 10 to 300 g of active substance per hectare (= g a.i./ha) for
25 component (b), preferably between 20 and 200 g a.i./ha, more particularly from 30 to 150 g a.i./ha.

For identical herbicidal activity, the application rate in the case of the combined application of herbicides (a)-(b) is substantially below the application rates for the
30 application of single applications of the herbicides of the type (a) or (b).

Consequently, particular interest attaches to stable formulations in which all active ingredients (a) and (b) with optional (c) are present, on the basis of their high biological activity – for an overall reduction in active ingredient content.

Nevertheless, the optimum choice of weight ratios and of application rates is

- 5 dependent on the development stage of the particular broadleaf or gramineous weeds, the prevailing weed spectrums, environmental factors, and climatic conditions, and so the weight ratios and application rates indicated above must be checked in each individual case.

- 10 The auxiliaries necessary for producing the stated formulations, such as, in particular, surfactants and solvents, are known in principle and are described, for example, in the following: McCutcheon's "Detergents and Emulsifiers Annual", MC Publ. Corp., Ridgewood N.J.; Sisley and Wood, "Encyclopedia of Surface active Agents", Chem. Publ.Co.Inc., N.Y. 1964; Schönfeldt, "Grenzflächenaktive
15 Äthylenoxidaddukte", Wiss. Verlagsgesellschaft, Stuttgart 1976; Winnacker-Küchler, "Chemische Technologie", volume 7, C. Hanser-Verlag, Munich, 4th edition 1986. Additional information is found in the presentations of the various companies providing components for agrochemical formulations.

- 20 Whereas the chemical "construction" of the individual components that can be employed is adequately described in such references, predictions concerning the properties of mixtures of such components for the formulation of a specific active ingredient system can generally not be inferred from the cited handbooks. When, for example, a surfactant/solvent combination is employed with which stable
25 emulsifiable concentrates are produced for active ingredient combinations of components (a) and (b) and optionally (c), at a relatively low "active ingredient loading", the products obtained when the active ingredient concentration is increased, in spite of the presence of surfactants, may no longer be stable concentrates, but instead may be unstable multiphase systems which also show a
30 tendency toward severe crystallization of the active ingredients. This is a direct indicator of the importance of components (d), (e), (f) and (g) of the invention. Generally speaking, the ECs of the invention comprise the active ingredients (a) to

(c) in dissolved form, and have to avoid crystallizing out of components at a range of temperature needed. Additionally, the components must achieve a ready formation of an emulsion when diluted with water, avoiding a separation or crystallizing out of the emulsion.

5

A factor critical for the selection of further surfactant components is their acidity or basicity per unit weight or volume, which is expressed by the acid number or amine number. Too sharp an increase in the total acid number or amine number in the ready-to-use formulation is problematic insofar as it may entail

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flocculation/crystallization of the formulated active ingredient(s). When selecting further surfactant components, consequently, it is necessary to ensure that the total acid number or amine number does not increase too sharply. Preferably, therefore, besides nonionic surfactants, only acidic or basic components with a sufficiently low acid or amine number are preferred. Since this number correlates, in turn, with the

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molecular weight, further surfactant components contemplated are in many cases also acidic or basic derivatives of compounds having a high molecular weight, such as tristyrylphenol alkoxyates, for example. In the case of nonionic surfactants, these considerations are irrelevant, in accordance with the nonionic nature of these components.

20

In this context it should additionally be noted that the surfactant/solvent systems of components (d) to (g) described permit the production of stable ECs having an active ingredient loading and composition that is variable within wide limits: accordingly, for example, the active ingredient loading of components (a)+(b) or (a)+(b)+(c),

25

respectively, is preferably of from 10 to 40, more preferably of from 15 to 30, particularly of from 20 to 25 percent by weight of the concentrated formulation.

Concentrated ECs produced in accordance with the present invention do not have or do not need additional water. Preferably they contain no water or only in very little

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amounts (less than 5%, preferably less than 3% water, more preferably less than 1% water based on the weight of the formulation) to ensure stability of the components (b) and (c) especially. The ECs usually contain minor amounts of residual water

present in the stated commercially available surfactants, surfactant mixtures and solvents. Owing to the surfactants present in the formulations, however, it is possible to dilute the stated formulations with water as far as a critical volume fraction, without this resulting in any clouding or destabilization of the formulation. The products in this case are, formally, first molecular solutions, then W/O microemulsions which on further increase in the water fraction undergo transition to W/O emulsions and lastly – on further dilution with water – to O/W emulsions. In addition to the surfactant/solvent mixture of components (d) to (g) of the invention, therefore, the invention also encompasses liquid formulations of the active ingredients (a), (b), and optionally (c) that comprise (additional) water as component (h).

More specifically, an object of the invention is an emulsifiable concentrate comprising

- (a) 1 to 35% by weight, preferably 5 to 25% by weight, particularly 8 to 20% by weight, metribuzin,
- (b) 1 to 20% by weight, preferably 2 to 15% by weight, particularly 4 to 12% by weight, herbicide selected from
 - (b1) esters of fenoxaprop-P and fenoxaprop,
 - (b2) esters of clodinafop,
 - (b3) pinoxaden,
- (c) optionally up to 20% by weight, optionally preferably 0.5 to 15% by weight, optionally particularly 1 to 3% by weight, other active ingredients, preferably safener mefenpyr-diethyl or cloquintocet-mexyl,
- (d) 5 to 80% by weight, preferably 10 to 60% by weight, particularly 15 to 55% by weight, more particularly 30 to 50% by weight, non-polar organic solvent,
- (e) 1 to 40% by weight, preferably 3 to 30% by weight, particularly 5 to 25% by weight, more particularly 10 to 20% by weight, polar organic co-solvent,
- (f) 1 to 60% by weight, preferably 2 to 50% by weight, particularly 5 to 40% by weight, more particularly 8 to 27% by weight, even more particularly 10 to 25% by weight,, one or more non-ionic emulsifiers,

- (g) 0.5 to 30% by weight, preferably 1 to 25% by weight, particularly 1 to 15% by weight, more particularly 2 to 10% by weight, one or more anionic emulsifiers, and
- (h) optionally up to 0.2 to 40% by weight, preferably optionally 0.5 to 30% by weight, optionally particularly 1 to 20% by weight, optionally more particularly 2 to 10% by weight, further formulation auxiliaries.

The emulsifiable concentrates (ECs) according to the invention are liquid formulations with a relatively high load of active ingredients and well storable at usual temperatures between 0°C and 50°C. The formulations are well stable against crystallizing out of the active ingredients, incompatibility of the active ingredients, their chemical degradation or phase separation of other ingredients.

The emulsifiable concentrates (ECs) according to the invention are liquid formulations which are simple to manufacture and low in cost. The ECs ensure a fast penetration of the combined active ingredients into the plants and provide the option for desired built-in adjuvants. They need only little agitation required to form the spray solution and are easy to prepare, handle and to apply for the farmer.

The emulsifiable concentrates according to the invention can be prepared, for instance, by dissolving the active compounds in the organic solvent (d) and adding the components (e) to (h) in any sequence and stirring. Other sequences of introducing the components (a) to (h) are also possible. The dissolving and mixing of the components may be accomplished in a standard apparatus such as a flask, bulb, vessel, tank or kettle equipped with a stirrer or mixer. To facilitate the dissolving or mixing steps, they may optionally be performed under moderately elevated temperature; usually below 100°C, preferably below 70°C. The preparation usually need not be performed under special anhydrous or water-free conditions.

The formulations and spray liquors produced with the surfactant/solvent system of the invention feature result in applications which are advantageous from the biological standpoint too. Hence it is observed that the biological activity of the active

ingredients (a) to (c) used in the formulations of the invention is boosted, in some cases synergistically.

The compositions according to the invention have an outstanding herbicidal activity against a broad spectrum of economically important monocotyledonous and dicotyledonous annual harmful plants. The active substances also act efficiently on perennial harmful plants which produce shoots from rhizomes, rootstocks or other perennial organs and which are difficult to control generally.

- 10 The formulations permit effective control of a sizable number of economically important weeds, particularly typical monocotyledonous and dicotyledonous weeds which occur also in cereal crops, examples being weeds of the following species: Alopecurus myosuroides, Avena fatua and other forms of wild oats, Lolium spp., Phalaris spp., Setaria spp., Echinochloa spp., Poa spp., Bromus spp., Elymus
15 repens, Sorghum spp. and others such as, for example, Agrostis, Panicum, etc.

Generally, weeds which can be controlled completely or partly, belong to:

- Monocotyledonous harmful plants of the genera: Aegilops, Agropyron, Agrostis, Alopecurus, Apera, Avena, Brachiaria, Bromus, Cenchrus, Commelina, Cynodon,
20 Cyperus, Dactyloctenium, Digitaria, Echinochloa, Eleocharis, Eleusine, Eragrostis, Eriochloa, Festuca, Fimbristylis, Heteranthera, Imperata, Ischaemum, Leptochloa, Lolium, Monochoria, Panicum, Paspalum, Phalaris, Phleum, Poa, Rottboellia, Sagittaria, Scirpus, Setaria, Sorghum.

- 25 Dicotyledonous weeds of the genera: Abutilon, Amaranthus, Ambrosia, Anoda, Anthemis, Aphanes, Artemisia, Atriplex, Bellis, Bidens, Capsella, Carduus, Cassia, Centaurea, Chenopodium, Cirsium, Convolvulus, Datura, Desmodium, Emex, Erysimum, Euphorbia, Galeopsis, Galinsoga, Galium, Hibiscus, Ipomoea, Kochia, Lamium, Lepidium, Lindernia, Matricaria, Mentha, Mercurialis, Mullugo, Myosotis,
30 Papaver, Pharbitis, Plantago, Polygonum, Portulaca, Ranunculus, Raphanus, Rorippa, Rotala, Rumex, Salsola, Senecio, Sesbania, Sida, Sinapis, Solanum,

Sonchus, Sphenoclea, Stellaria, Taraxacum, Thlaspi, Trifolium, Urtica, Veronica, Viola, Xanthium.

- Examples of specific species of such weeds are *Abutilon indicum*, *Acalypha indica*,
 5 *Acanthosporium hispidum*, *Aeschynomene indica*, *Ageratum conyzoides*, *A.*
Hustionium, *Agropyron repens*, *Alhagi camelorum*, *Allium vineale*, *Alternanthera*
pungens, *A. Sessiles*, *Amaranthus gracilis*, *A. viridis*, *A. spinosus*, *A. hybridus*,
Anagallis arvensis, *Araemone Mexicana*, *Asphodelus tenuifolius*, *Avena ludoviciana*
 10 *, Bidens pilosa*, *Boerhavia diffusa*, *Brachiaria rutica*, *B. distachya stanf.*, *Brassica*
arvensis, *Bulbostylis barbata*, *Calotropis gigantea*, *C. procera*, *Cannabis sativa*,
Carthamus oxyantha, *Cassia occidentalis*, *Cassia auriculata*, *Catharanthus*
pussilus, *Calosia arcuatea*, *Ceratophyllum demersum*, *Chara* spp., *Chenopodium*
album, *Chenopodium murale*, *Chloris barbata*, *Cichorium intybus*, *Cirsium arvense*,
Cleome viscosa, *Cleome rutidosperma*, *Commelina benghalensis*, *Convolvulus*
 15 *arvensis*, *Conyza canadensis*, *Corchorus olitorius*, *Corchorus aestivus*, *Corchorus*
trilocularis, *Corchorus tridens*, *Capsularis*, *Coronopus didymus*, *Crocalaria medica*,
Crocalaria burhia, *Croton sparsiflorus*, *Cucumis trigonus*, *Cuscuta reflexa*, *Cynodon*
dactylon, *Cyperus compactus*, *Cyperus imbricatus*, *Cyperus iria*, *Cyperus rotundus*,
Cyperus Compressus, *Cyperus difformis*, *Cyperus kylinga*, *Cyperus esculentus*,
 20 *Dactylcarenium aegyptium*, *Datura stramonium*, *Desmostachya bipinnata*, *Digera*
arvensis, *Digitaria ciliaris*, *Digitaria adscendens*, *Digitaria setigera*, *Echinochloa crus*
galli, *Echinochloa colonum*, *Eclipta alba*, *Eichhornia crassipes*, *Eleusine indica*,
Eragrostis ciliaris, *Eragrostis japonica*, *Erigeron canadensis*, *Euphorbia*
dracunculoides, *Euphorbia hirta*, *Euphorbia thymifolia*, *Euphorbia microphylla*,
 25 *Fimbristylis tenera*, *Fumaria parviflora*, *Gomphirana celosioides*, *Heliotropium*
eichwaldi, *Heliotropium indicum*, *Hydrilla verticillata*, *L. pestigridis*, *Ischaemum*
rugosum, *Kochia scorpioides*, *Lantana camara*, *Lathyrus phaeus*, *Lunea asplenifolia*,
Lunea nudicaulis, *Leucilia aspara*, *Lolium temulentum*, *Leptochloa Phleoides*,
Ludwigia parennis, *Medicago dentuculata*, *Mycopoyllum spicatum*, *Nelumbo*
 30 *nucifera*, *Nymphaea odorata*, *Oldedlemia conymbosa*, *Opuntia dillemir*, *Orabanche*
aegyptica, *Orabanche micotina*, *Oryza sativa*, *Oxalis corniculata*, *Panicum maximum*,
Panicum repens, *Parthenium hysterophorus*, *Paspalum distichum*, *Paspalum*

Sanquinale, Pennisetum purpureum, Phalaris minor, Phyllanthus niruri, Pistia
 soratiotes, Pluchea lanceolata, Poannua, Polygonum fanigerum, Polygonum
 plebijem, Polygonum barbatum, Polygonum glabrum, Polypogan monspeliensis,
 Portulaca oleraeae, Portulaca quadrifida, Potamogeton pectinantus, Potamogeton
 5 crispus, Potamogeton perfoliatus, Potamogeton nodosus poir, Pupalia lappaceae,
 Rumex maritimus, Saccharum spontaneum, Saccharum munio, Salvinia auriculata,
 Saponaria vaccaria, Setaria glauca, Setaria verticillata, Silene conoidea, Sisymbrium
 irio, Solanum nicrum, Solanum xanthocarpum, Sonchus arvensis, Sonchus
 oleraceus, Sorghum halepense, Spergula arvensis, Sporobolus diadrer, Sporobolus
 10 poiretti, Stellaria media, Striga euphrasioides, Striga densiflora, Tephrosia purpurea,
 Trianthema portulacastrum, Trianthema morogyne, Tribulus terrestris, Trigonella
 polycerata, Trigonella incisa Benth, Typha angustata, Typha latifolia, Vallisneria
 spiralis, Vernonia cinerea, Vicia sativa, Vicia hirsuta, Vicoa indica, Xanthium
 strumarium.

15

Although the co-formulations according to the invention display an outstanding
 herbicidal activity against monocotyledonous and dicotyledonous weeds, crop plants
 of economically important crops, for example cereal crops such as Avena (oats),
 Hordeum (barley), Oryza (rice), Panicum, Saccharum, Secale (rye), Sorghum
 20 (millet), Triticale, Triticum (wheat), Zea (maize), are damaged only to an insignificant
 extent, or not at all, depending on the structure of the respective components and its
 application rate. This is why the compositions are highly suitable for the selective
 control of undesired plant growth in plant crops such as cereal crops, particularly in
 crops such as Triticum (wheat), Secale (rye), Hordeum (barley) and Triticale, more
 25 particularly Triticum.

The present invention therefore also relates to a method of controlling unwanted
 plants or for regulating the growth of plants, preferably in crops of plants, wherein an
 effective amount of the herbicidal composition according to the invention, optionally
 30 or usually after dilution with water, is applied to the plants (for example including
 harmful plants such as monocotyledonous or dicotyledonous weeds in the presence
 of crop plants), to the seeds (for example grains, seeds or vegetative propagules

such as tubers or shoot parts with buds) or to the area on which the plants grow (for example the area under cultivation). In this context, the compounds according to the invention can be applied for example pre-planting (if appropriate also by incorporation into the soil), pre-emergence or post-emergence.

5

If the compounds according to the invention are applied to the soil surface before germination, either the emergence of the weed seedlings is prevented completely or the weeds grow until they have reached the cotyledon stage, but then stop their growth and, finally, die completely after three to four weeks have elapsed.

10

When the active substances are applied post-emergence to the green plant parts, growth stops after the treatment, and the harmful plants remain in the growth stage of the time of application or die fully after a certain period of time, so that competition by weeds, which is harmful to the crop plants, is thus eliminated at an early point in time and in a sustained manner.

15

Due to the active ingredients combined and the other formulation components the co-formulations provide an improved weed control at reduced phytotoxicity to the crop compared with metribuzin alone or many tank-mixtures.

20

A) Preparation Examples

The formulations as shown in the Tables 1, 2 and 3 below were obtained by dissolving or mixing the components a), b) and c) in the organic solvent d) and then introducing the components e), f) and g) under mixing in a standard apparatus. In some cases the dissolving or mixing was facilitated by raising the temperature slightly (not exceeding 60°C).

25

In the Examples below, quantities are given by weight, unless indicated otherwise.

30

Table 1: Stable emulsifiable concentrates

[illegible]

Table 1 (continued)

Component	Type/ group	Composition No.							
		8	9	10	11	12	13	14	15
Fenoxaprop-P-Et	(B1.1)	7.76	7.76	7.76	7.76	3.91	3.91	6.95	7.76
Mefenpyr-diethyl	(C1.1)	1.94	1.94	1.94	1.94	0.98	0.98	1.73	1.94
Metribuzin	(A1)	13.59	13.59	13.59	12.04	13.70	8.21	12.04	13.59
Emulsogen EL 400	(f)	5.00	5.00	0.00	5.00	5.00	5.00	5.00	5.00
Emulsogen 3510	(f)	0.00	0.00	5.00	0.00	0.00	0.00	0.00	0.00
Emcol P 1860	(g)	0.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00
Atplus 309F LM	(f)+(g)	10.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Genagen 4166	(e)	15.00	15.00	15.00	15.00	15.00	15.00	15.00	5.00
Rhodacal 60 BE	(g)	5.00	0.00	0.00	5.00	5.00	5.00	5.00	5.00
Genapol X-060	(f)	0.00	10.00	0.00	10.00	10.00	10.00	0.00	10.00
Arkopal N-100	(f)	0.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00
Sapogenat T-300	(f)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Genapol C 100	(f)	0.00	0.00	10.00	0.00	0.00	0.00	0.00	0.00
Genapol PF-10	(f)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Soprophor 796/P	(f)	5.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00
Soprophor BSU	(f)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Soprophor S/25	(f)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triton GR 7ME	(g)	0.00	0.00	10.00	0.00	0.00	0.00	0.00	0.00
Solvesso 200 ND	(d)	36.71	36.71	36.71	43.26	46.41	51.90	44.28	51.71

Table 1 (continued)

Component	Type/ group	Composition No.							
		M8	M9	M10	M11	M12	M13	M14	M15
Fenoxaprop-P-Et	(B1.1)	7.76	7.76	7.76	7.76	3.91	3.91	6.95	7.76
Mefenpyr-diethyl	(C1.1)	1.94	1.94	1.94	1.94	0.98	0.98	1.73	1.94
Metribuzin	(A1)	13.59	13.59	13.59	12.04	13.70	8.21	12.04	13.59
Emulsogen EL 400	(f)	5.00	5.00	0.00	5.00	5.00	5.00	5.00	5.00
Emulsogen 3510	(f)	0.00	0.00	5.00	0.00	0.00	0.00	0.00	0.00
Emcol P 1860	(g)	0.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00
Atplus 309F LM	(f)+(g)	10.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Genagen 4166	(e)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Rhodacal 60 BE	(g)	5.00	0.00	0.00	5.00	5.00	5.00	5.00	5.00
Genapol X-060	(f)	0.00	10.00	0.00	10.00	10.00	10.00	0.00	10.00
Arkopal N-100	(f)	0.00	0.00	0.00	0.00	0.00	0.00	10.00	0.00
Sapogenat T-300	(f)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Genapol C 100	(f)	0.00	0.00	10.00	0.00	0.00	0.00	0.00	0.00
Genapol PF-10	(f)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Soprophor 796/P	(f)	5.00	5.00	0.00	0.00	0.00	0.00	0.00	0.00
Soprophor BSU	(f)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Soprophor S/25	(f)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Triton GR 7ME	(g)	0.00	0.00	10.00	0.00	0.00	0.00	0.00	0.00
Solvesso 200 ND	(d)	51.71	51.71	51.71	51.26	51.41	66.90	59.28	56.71

Abbreviations for Table 1: see next page

Abbreviations for Table 1:

Arkopal® N-100	=	nonylphenol polyglycol ether with 10 EO (f1.2)
Atplus® 309 F LM	=	mixture of 80% sorbitan trioleate ethoxylate(Tween® 85) (f2.6) and 15% sorbitan monooleate (Span® 80) (f2.6) and 5% dodecylbenzolsulfonate isopropylammonium salt (g1.2)
Emcol® P 1860	=	branched dodecylbenzolsulfonate calcium salt, 60% in n-octanol (g1.2)
Emulsogen® EL 400	=	ethoxylated castor oil with 40 EO (f2.2)
Emulsogen® 3510	=	EO/PO blockcopolymer waxy (= butanol alkoxyated with EO and PO) (f2.11)
Fenoxaprop-P-Et	=	Fenoxaprop-P-ethyl (common name) (b)
Genagen® 4166	=	mixture of N,N-dimethyl-(C ₈ /C ₁₀)alkanamides (e4)
Genapol® X-060	=	ethoxylated isotridecyl alcohol with 6 EO (f2.1)
Genapol® C 100	=	coconut fatty alcohol polyglycol ether with 10 EO (f2.1)
Genapol® PF-10	=	EO/PO blockpolymer, EO _x PO _y EO _z having 10% EO (f2.10)
Rhodacal® 60 BE	=	dodecylbenzolsulfonate-calcium, 60% in 2-ethyl-hexanol (g1.2)
Sapogenat® T-300	=	Tri-sec-butylphenol polyglycol ether with 30 EO (f1.2)
Solvesso® 200 ND	=	organic solvent, mixture of C ₉ -C ₁₁ -aromatic hydrocarbon, naphtalene depleted (b.p. 219-282°C) (d)
Soprophor® 796/P	=	alkoxylated tristyrylphenol with 4 PO and 20 EO (f1.3)
Soprophor® BSU	=	ethoxylated tristyrylphenol with 16 EO (f1.3)
Soprophor® S/25	=	ethoxylated tristyrylphenol with 25 EO (f1.3)
Triton® GR 7ME	=	dioctylsulfosuccinate sodium salt (64%) in aromatic hydrocarbon solvent (g2.3)

Table 2: Emulsifiable concentrates for solvent test

Component	Type / group	Composition No.					
		16	17	18	19	20	21
Fenoxaprop-P-ethyl	(B1.1)	7.76	7.76	7.76	7.76	7.76	7.76
Mefenpyr-diethyl	(C1.1)	1.94	1.94	1.94	1.94	1.94	1.94
Metribuzin	(A1)	13.59	13.59	13.59	13.59	13.59	13.59
Acetophenone	(e)	15.00	0.00	0.00	0.00	0.00	0.00
γ -Butyrolactone	(e)	0.00	15.00	0.00	0.00	0.00	0.00
Cyclohexanone	(e)	0.00	0.00	15.00	0.00	0.00	0.00
Genagen 4166	(e)	0.00	0.00	0.00	15.00	0.00	0.00
NOP ¹⁾	(e)	0.00	0.00	0.00	0.00	15.00	0.00
Tetrahydrofurfuryl alcohol	(e)	0.00	0.00	0.00	0.00	0.00	15.00
Non-ionic surfactant ²⁾	(f)	20.00	20.00	20.00	20.00	20.00	20.00
Anionic surfactant ³⁾	(g)	5.00	5.00	5.00	5.00	5.00	5.00
Solvesso 200 ND	(d)	36.71	36.71	36.71	36.71	36.71	36.71

Table 2 (continued)

Component	Type / group	Composition No.		
		22	23	24
Fenoxaprop-P-ethyl	(B1.1)	7.76	7.76	7.76
Mefenpyr-diethyl	(C1.1)	1.94	1.94	1.94
Metribuzin	(A1)	13.59	13.59	13.59
Acetophenone	(e)	0.00	0.00	0.00
γ -Butyrolactone	(e)	0.00	0.00	0.00
Cyclohexanone	(e)	0.00	0.00	0.00
Genagen 4166	(e)	5.00	10.00	0.00
NOP ¹⁾	(e)	0.00	0.00	0.00
Tetrahydrofurfuryl alcohol	(e)	0.00	0.00	0.00
Non-ionic surfactant ²⁾	(f)	20.00	20.00	20.00
Anionic surfactant ³⁾	(g)	5.00	5.00	5.00
Solvesso 200 ND	(d)	46.71	41.71	51.71

Abbreviations for Table 2:

see abbreviations for Table 1 and

¹⁾ NOP = N-octylpyrrolidone

²⁾ A blend of non-ionic surfactants of group (f) (same for all examples 16-24)

³⁾ An anionic surfactant of group (g) (same for all examples 16-24)

Table 3

Component	Type / group	Composition No.			
		25	26	27	28
Clodinafop-propagyl	(B2.1)	5.82	0.00	5.82	0.00
Pinoxaden	(B3.1)	0.00	5.82	0.00	5.82
Mefenpyr-diethyl	(C1.1)	0.00	0.00	1.45	1.45
Cloquintocet-mexyl	(C2.1)	1.45	1.45	0.00	0.00
Metribuzin	(A1)	13.59	13.59	13.59	13.59
Polar co-solvent ^(A)	(e)	15.00	15.00	15.00	15.00
Non-ionic surfactant ^(B)	(f)	20.00	20.00	20.00	20.00
Anionic surfactant ^(C)	(g)	5.00	5.00	5.00	5.00
Solvesso 200 ND	(d)	39.14	39.14	39.14	39.14

Abbreviations for Table 3:

see abbreviations for Tables 1 and 2, and

- (A) A polar co-solvent of group (e) (same for all examples 25-28)
- (B) A blend of non-ionic surfactants of group (f) (same for all examples 25-28)
- (C) An anionic surfactant of group (g) (same for all examples 25-28)

B) Stability tests

B1) Application test (CIPAC)

The formulations according to Table 1 of section A) above were tested according to their applicability for preparing a chemically and physically stable spray liquor. The test method is a standard according to CIPAC (COLLABORATIVE INTERNATIONAL PESTICIDES ANALYTICAL COUNCIL). All the formulations 1-15 had a positive CIPAC test result. Contrary to examples no. 1 to 15, the example mixtures M1 to M15 (comparisons) did not give a stable formulation but two-phase mixtures where metribuzin had not been dissolved significantly.

CIPAC Method MT 36.1, see CIPAC Content Handbook F

“EMULSION CHARACTERISTICS OF EMULSIFIABLE CONCENTRATES”

15 Outline of Method:

100 ml of aqueous emulsion (five per cent v/v oil phase when diluted). The stability of this emulsion is then in terms of the amounts of free 'oil' or 'cream' which separates while the emulsion is allowed to stand undisturbed for 24 h. The ability of the system to re-emulsify at the end of the 24 h period is also determined.

20

Scope:

The procedure described in this method is applicable to any emulsifiable concentrate, which gives rise, on dilution with water, to oil in water emulsions.

25

B2) Stability at low temperature

The formulations according to Table 1 of section A) above were tested according to their stability against crystallization or phase separation at 0°C for 1 week. The temperature was then raised up to ambient temperature and tested after 1 day for phase separation. The results are shown in Table 4 (first line indicates the formulation as numbered according to Table 1 above, second and third line indicate the result in the test):

Table 4: Stability test at 0°C

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
A ¹⁾	-	-	-	+	-	+	+	-	-	+	-	-	-	-	++
B ²⁾	-	-	-	-	-	-	-	-	-	-	-	-	-	-	++

Abbreviations in Table 4:

5 1) test after 1 week at 0°C

2) test after one day at ambient temperature

"-" means clear formulation

"+" means cloudy formulation

"++" means crystallization (visible crystals formed)

10

Results:

The formulations 1 to 14 are practically useful formulations. Some of them become cloudy at low temperatures indicating tendency of separation. The cloudiness can be resolved within 1 day at ambient temperature. Only the formulations of no. 15 of

15 Table 1 with insufficient content of polar organic co-solvent produced crystals at 0°C, showing severe separation which did not resolve after one day at ambient temperature.

20 B3) Chemical stability at elevated temperature

The formulations according to Table 1 of section A) above were tested according to their stability against chemical degradation at 54°C for two weeks. The breakdown (in percent) of the active ingredient fenoxaprop-P-ethyl was measured as an

25 indication of the stability. The results are shown in Table 5 (first line indicates the formulation as numbered according to Table 1 above, second line indicates the result obtained in the test):

Table 5: Stability test (chemical stability) at 54°C

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
-3.2	-3.9	-3.2	-3.0	-5.9	-2.4	-3.5	-9.8	-2.1	-0.5	-2.9	-2.7	-2.9	-2.5	-1.4

The chemical degradation of Metribuzin and Mefenpyr(-diethyl) is negligible.

5

B4) Stability comparison of formulations of Table 2

10 The formulations according to Table 2 of section A) above were prepared and tested according to their stability against crystallization or phase separation at ambient temperature and at 0°C for 1 week. The formulations of nos. 16 to 21 of Table 2 with various different polar organic co-solvents were stable without phase separation (no clouding) and no crystals, even at 0°C.

15 The formulation of no. 15 of Table 1, and formulations of nos. 22 and 23 of Table 2 with insufficient content of polar organic co-solvent produced crystals at 0°C. The formulation no. 24 of Table 2 without polar organic co-solvent did not form an emulsifiable concentrate (solution), even at ambient temperature.

C) Biological Examples

C1) Free range trial, control of harmful plants by the post-emergence method

5 In free-range trials, seed of wheat and *Phalaris minor* (PHAMI, monocot), *Rumex maritimus* (RUMMA, dicot) and *Chenopodium album* (CHEAL, dicot), respectively, were sown and grown in soils of different type to evaluate practical weed control conditions. The formulations according to Table 1 of section A) above were diluted with water and applied to the infested wheat fields after emergence of the plants
10 under the following conditions:

Application rate: 175 g/ha Metribuzin + 100 g/ha Fenoxaprop-P-ethyl + 25 g/ha Mefenpyr-diethyl;

Water volume: 200-400 l/ha by sprayer having flood jet nozzle

Application time: PHAMI at 2-5 leaf stage; wheat 38 days after sowing, BBCH
15 stage 22-23 (2-3 tillers detectable)

weed count/m²: 50 - 212

The effectiveness of the herbicide treatments was scored visually in comparison with an untreated control, the assessment being carried out using a percent scale
20 (0-100% efficacy).

Results:

The control of dicot weed CHEAL was in the range of 90-95%, the control of dicot weed RUMMA was in the range of 80 to 85% and the control of monocot PHAMI was
25 in the range of 83 to 87%. The damage to the wheat plants was neglectible. The formulations were shown to be useful for effectively controlling weeds in wheat crops.

Patent claims

1. A liquid herbicidal emulsifiable concentrate comprising
 - (a) the herbicidal active substance metribuzin,
 - 5 (b) one or more herbicidal active substances selected from the group consisting of the ACCase inhibitors (b1), (b2) and (b3):
 - (b1) esters of fenoxaprop-P and esters of fenoxaprop,
 - (b2) esters of clodinafop,
 - (b3) pinoxaden,
 - 10 (c) optionally other active ingredients, which do not substantially interfere with the stability of the co-formulation,
 - (d) one or more non-polar organic solvents,
 - (e) one or more polar organic co-solvents,
 - (f) one or more non-ionic emulsifiers,
 - 15 (g) one or more anionic emulsifiers, and
 - (h) optionally further formulation auxiliaries.
2. The concentrate as claimed in claim 1, characterized in comprising
 - (a) 1 to 35% by weight metribuzin,
 - 20 (b) 1 to 20% by weight of one or more herbicides selected from (b1), (b2) and (b3):
 - (b1) esters of fenoxaprop-P and esters of fenoxaprop,
 - (b2) esters of clodinafop,
 - (b3) pinoxaden,
 - 25 (c) optionally up to 20% by weight other active ingredients which do not substantially interfere with the stability of the co-formulation,
 - (d) 5 to 80% by weight one or more non-polar organic solvents,
 - (e) 1 to 40% by weight one or more polar organic co-solvents,
 - (f) 1 to 60% by weight one or more non-ionic emulsifiers,
 - 30 (g) 0.5 to 30% by weight one or more anionic emulsifiers, and
 - (h) optionally up to 0.2 to 40% by weight further formulation auxiliaries.

3. The concentrate as claimed in claim 1 or 2, characterized in comprising fenoxaprop-P-ethyl, clodinafop-propargyl, pinoxaden or a mixture thereof as component (b).

5 4. The concentrate as claimed in claim 1 or 2, characterized in fenoxaprop-P-ethyl as component (b).

5. The concentrate as claimed in any of claims 1 to 4, characterized in comprising mefenpyr-diethyl or cloquintocet-mexyl as component (c).

10

6. The concentrate as claimed in in any of claims 1 to 4, characterized in comprising fenoxaprop-P-ethyl as component (b) and mefenpyr-diethyl as component (c).

15 7. The concentrate as claimed in any of claims 1 to 6, characterized in comprising a non-polar organic solvent selected from aliphatic hydrocarbons, aromatic hydrocarbons, halogenated aliphatic hydrocarbons, halogenated aromatic hydrocarbons and mixtures thereof as component (d).

20 8. The concentrate as claimed in any of claims 1 to 6, characterized in comprising a non-polar organic solvent selected from aliphatic hydrocarbons, aromatic hydrocarbons and mixtures thereof as component (d).

25 9. The concentrate as claimed in any of claims 1 to 8, characterized in comprising a polar organic co-solvent selected from the group consisting of lipophilic alcohols, esters, ethers, N,N-dialkylated carboxylic acid amides having 1-18 carbon atoms in the carboxylic acid moiety, cyclic amides, ketones, nitriles, phosphates, sulfoxides and sulfones, oils and mixtures of the afore-mentioned co-solvents as component (e).

30

10. The concentrate as claimed in any of claims 1 to 9, characterized in comprising a polar organic co-solvent selected from the group consisting of

lipophilic alcohols, esters, N,N-dialkylated carboxylic acid amides having 1-18 carbon atoms in the carboxylic acid moiety, cyclic amides, ketones and mixtures of the afore-mentioned co-solvents as component (e).

- 5 11. The concentrate as claimed in any of claims 1 to 10, characterized in comprising one or more non-ionic emulsifiers selected from the group consisting of aromatic-based and non-aromatic non-ionic surfactants in combination with one or more anionic emulsifiers selected from the group consisting of aromatic-based and non-aromatic based anionic surfactants.
- 10 12. The concentrate as claimed in claim 11, characterized in comprising a non-ionic emulsifier selected from the group consisting of phenyl (C₁-C₄)alkyl ethers or (poly)alkoxylated phenols, (poly)alkylphenols or (poly)alkylphenol alkoxylates, poly(arylalkyl)-phenols, poly(arylalkyl)-phenol
- 15 alkoxylates, fatty alcohol alkoxylates, fatty acid alkoxylates, triglyceride alkoxylates, fatty acid amide alkoxylates, fatty amine alkoxylates, alkylene oxide adducts of alkandiol, sugar derivatives, sorbitan esters, cyclodextrin esters, cellulose derivatives, algin-, pectin- and guar derivatives, alkylene oxide adducts on a polyol basis, polyglycerides and their derivatives, silicones or silanes, copolymers
- 20 consisting of EO, PO and/or BO units, alkylene oxide adducts of C₁-C₉ alcohols, polyvinyl compounds, polymers based on maleic anhydride.
13. The concentrate as claimed in claim 11, characterized in comprising a non-ionic emulsifier selected from the group consisting of
- 25 (poly)alkylphenols or (poly)alkylphenol alkoxylates, poly(arylalkyl)-phenols, poly(arylalkyl)-phenol alkoxylates, fatty alcohol alkoxylates, fatty acid alkoxylates, triglyceride alkoxylates, sorbitan esters, copolymers consisting of EO, PO and/or BO units and alkylene oxide adducts of C₁-C₉ alcohols.
- 30 14. The concentrate as claimed in claim 11, characterized in comprising an anionic emulsifier selected from the group consisting of

phosphated or sulfated phenyl (C₁-C₄)alkyl ethers, phosphated or sulfated (poly)alkoxylated phenols, phosphated or sulfated (poly)alkylphenols, phosphated or sulfated (poly)alkylphenol alkoxylates, phosphated or sulfated poly(arylalkyl)-phenols, phosphated or sulfated poly(arylalkyl)-phenol alkoxylates, (poly)alkyl- and poly(arylalkyl)-benzenesulfonates in acidic or salt form, ether carboxylates, sulfonates, sulfates and phosphates of fatty alcohol alkoxylates or of fatty acid alkoxylates, salts of carboxylic acids, salts of polycarboxylic acids, alpha-sulfo fatty acid esters, sulfosuccinates, alkanesulfonates, paraffinsulfonates, olefinsulfonates, sulfosuccinamates, polyacrylic and polymethacrylic derivatives.

10

15. The concentrate as claimed in claim 11, characterized in comprising an anionic emulsifier selected from the group consisting of phosphated or sulfated (poly)alkylphenol alkoxylates, phosphated or sulfated poly(arylalkyl)-phenol alkoxylates, (poly)alkyl- and poly(arylalkyl)-benzenesulfonates in acidic or salt form and sulfosuccinates.

15

16. The concentrate as claimed in any of claims 1 to 15, characterized in comprising further formulation auxiliaries of other type selected from the group consisting of further solvents, further surfactants, agents which influence the thixotropy and rheology of the emulsifiable concentrates, frost preventatives, evaporation inhibitors, preservatives, odorants, colorants, defoamers, fillers, carriers, dyes and pH-modifiers.

20

17. A process for preparing the concentrate as defined in any of claims 1 to 16, which comprises mixing the components (a) to (h).

25

18. A method of controlling unwanted plant growth, which comprises applying an effective amount of the liquid concentrate as claimed in any of claims 1 to 16, optionally after dilution with water, to the plants, to the seeds or to the area on which the plants grow.

30

19. The method as claimed in claim 18, characterized in that weed plants are controlled selectively in crops.

20. The method as claimed in claim 19, characterized in that the crop is a cereal.

5

21. Use of the liquid concentrate as claimed in any of claims 1 to 16 for weed control, optionally for selective weed control in crops.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/054268

A. CLASSIFICATION OF SUBJECT MATTER

INV. A01P13/00 A01P13/02 A01N25/02 A01N43/707 A01N43/76
A01N43/40 A01N43/90

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

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, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 823 995 A1 (HOECHST SCHERING AGREVO GMBH [DE] BAYER CROPSOURCE AG [DE]) 18 February 1998 (1998-02-18) cited in the application claims 1-8 last paragraph on p. 8, example 4 page 4, line 47 - line 53; claim 4 -----	1-21
Y	EP 0 614 608 A2 (HOECHST SCHERING AGREVO GMBH [DE]) 14 September 1994 (1994-09-14) cited in the application claim 4; table 1 page 5, paragraph 6 ----- -/-	1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2012/054268

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	YADAV ASHOK ET AL: "Effect of dithiopyr alone and as tank mixture with other herbicides against weeds in wheat", ENVIRONMENT AND ECOLOGY, MKK PUBLICATION, CALCUTTA, IN, vol. 24s, no. Suppl. 3A, 1 January 2006 (2006-01-01), pages 853-856, XP009151937, ISSN: 0970-0420 cited in the application table 1 abstract -----	1-21

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/054268

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