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(54) Title: EMULSIFIABLE HERBICIDAL COMPOSITION

(57) Abstract: An emulsifiable herbicidal composition comprising Pinoxaden, a compound of formula (I) as solvent, and the use of the compound of formula (I) in inhibiting the decomposition of Pinoxaden in emulsifiable compositions.

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EMULSIFIABLE HERBICIDAL COMPOSITION

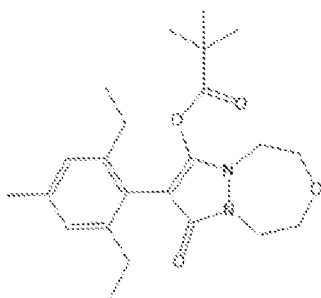
[0001] This application claims priority filed on 24 July 2020 in INTERNATIONAL PROCEDURE with Nr PCT/CN2020/103998, the whole content of this application being incorporated herein by reference for all purposes.

FIELD OF THE INVENTION

[0002] The present invention relates to an emulsifiable herbicidal composition comprising Pinoxaden and a compound of formula (I) as solvent. In addition, the present invention also relates to the use of the compound of formula (I) in inhibiting the decomposition of Pinoxaden in the herbicidal emulsifiable compositions.

BACKGROUND OF THE INVENTION

[0003] Pinoxaden is the common name of the herbicide 8-(2,6-diethyl-4-methylphenyl)-7-oxo-1,2,4,5-tetrahydro-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl pivalate [8-(2,6-diethyl-4-methylphenyl)-7-oxo-1,2,4,5-tetrahydropyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl]- 2,2-dimethyl propanoate. It is a pro-herbicide (by hydrolysis of the pivalate ester to give the corresponding enol) and is used for control of grass weeds in cereal crops such as wheat, barley and rye crops.



Pinoxaden

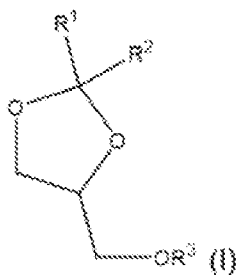
[0004] Emulsifiable concentrates of Pinoxaden are disclosed in WO07073933 A2 which addresses the stability of the compositions, particularly in relation to decomposition, hydrolysis or transesterification. The emulsifiable concentrate compositions are said to have improved stability by virtue of the use of certain alcohol solvents and in particular tetrahydrofurfuryl alcohol. The commercial product "Axial 100 EC" selective herbicide available from Syngenta (Axial is a trademark of Syngenta) contains 10 wt.% Pinoxaden and 20 to 40 wt.% tetrahydrofurfuryl alcohol.

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- [0005] In 2017, tetrahydrofurfuryl alcohol was classified as carcinogenic, mutagenic, or reprotoxic (CMR) category 1A and 1B by European Commission (EC), thereby restricting its manufacture, placing on the market, or use.
- [0006] Emulsifiable concentrates (also referred to as EC) are widely used formulations in crop protection. The disadvantage of the known emulsifiable concentrates is the poor low temperature stability, in other words, the pronounced tendency to crystallize at low temperature.
- [0007] Therefore, it is still desirable to develop an emulsifiable herbicidal composition comprising Pinoxaden as active ingredient, which eliminates CMR risks but has comparable or even better decomposition inhibition performance, meanwhile has better low temperature stability.

SUMMARY OF THE INVENTION

- [0008] It is an objective of the present invention to provide an emulsifiable herbicidal composition comprising Pinoxaden as active ingredient, which eliminates CMR risks but has comparable or even better decomposition inhibition performance, meanwhile has better low temperature stability.
- [0009] The emulsifiable herbicidal composition as provided in the present invention comprises:
- a) an agricultural active ingredient of Pinoxaden in an amount from 0.5 to 50 wt.%, based on the total weight of the emulsifiable herbicidal composition;
 - b) a solvent selected from a compound of formula (I) in an amount from 1 to 90 wt.%, based on the total weight of the emulsifiable herbicidal composition,



wherein,

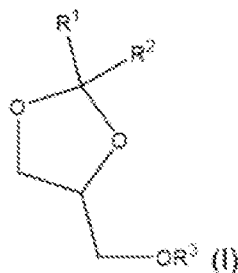
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R¹ and R² are each independently selected from linear or branched C₁-C₁₂ alkyl, C₄-C₁₂ cycloalkyl or aryl; and

R³ is selected from H, linear or branched alkyl, cycloalkyl or a -C(=O)R⁴ group, with R⁴ being selected from a linear or branched alkyl or cycloalkyl.

- [0010] In one embodiment of the present invention, the emulsifiable herbicidal composition further comprises one or more emulsifiers selected from the group consisting of non-ionic surfactant and anionic surfactant.
- [0011] In another one embodiment of the present invention, the herbicidal composition further comprises one or more herbicides selected from the group consisting of triasulfuron, tribenuron, metsulfuron, thifensulfuron, flupyrsulfuron, chlorsulfuron, prosulfuron, amidosulfuron, mesosulfuron, sulfosulfuron, tritosulfuron, clodinafop-propargyl, fenoxaprop-P-ethyl, diclofop-methyl, cyhalofop-butyl, florasulam, metosulam, flumetsulam, dicamba, clopyralid, an ester of 2,4-D, 2,4-DP, mecoprop, mecoprop-P, MCPA, MCPB, dichlorprop-P, fluroxypyr, tralkoxydim, triallate, prosulfocarb, bromoxynil, bromoxynil octanoate, ioxynil, ioxynil octanoate, pendimethalin, trifluralin, and diflufenican.
- [0012] In yet another one embodiment of the present invention, the emulsifiable herbicidal composition is an emulsifiable concentrate or an oil dispersible suspension.
- [0013] In another aspect, the present invention provides a dilution of the emulsifiable herbicidal composition prepared by diluting the emulsifiable herbicidal composition with aqueous medium for 10 to 2000 times.
- [0014] In yet another aspect, the present invention provides a method of controlling the growth of unwanted plants, comprising a step of applying to the plants or to the locus of unwanted plant an effective amount of the dilution of the emulsifiable herbicidal composition.
- [0015] In yet another aspect, the present invention provides a use of a compound of formula (I) in inhibiting the decomposition of Pinoxaden in emulsifiable herbicidal compositions,

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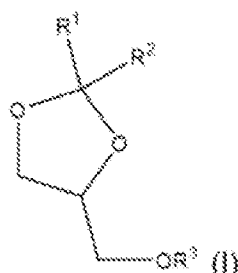


wherein

R^1 and R^2 are each independently selected from linear or branched C_1 - C_{12} alkyl, C_4 - C_{12} cycloalkyl or aryl; and

R^3 is selected from H, linear or branched alkyl, cycloalkyl or a $-C(=O)R^4$ group, with R^4 being selected from a linear or branched alkyl or cycloalkyl.

[0016] In still yet another aspect, the present invention provides a compound of formula (I) as a solvent for preparing emulsifiable herbicidal compositions comprising an agricultural active ingredient of Pinoxaden,



wherein

R^1 and R^2 are each independently selected from linear or branched C_1 - C_{12} alkyl, C_4 - C_{12} cycloalkyl or aryl; and

R^3 is selected from H, linear or branched alkyl, cycloalkyl or a $-C(=O)R^4$ group, with R^4 being selected from a linear or branched alkyl or cycloalkyl.

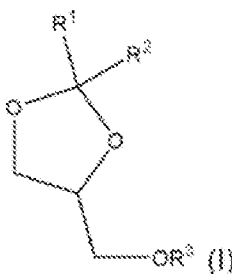
DETAILED DESCRIPTION

[0017] Throughout the description, including the claims, the term "comprising one" or "comprising a" should be understood as being synonymous with the term "comprising at least one", unless otherwise specified. The terms "between" and "from ... to..." should be understood as being inclusive of the limits.

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- [0018] The articles “a”, “an” and “the” are used to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article.
- [0019] It should be noted that in specifying any range of concentration, weight ratio or amount, any particular upper concentration, weight ratio or amount can be associated with any particular lower concentration, weight ratio or amount, respectively.
- [0020] As used herein, the term “alkyl” means a saturated hydrocarbon radical, which may be linear, branched or cyclic, such as, methyl, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, t-butyl, pentyl, n-hexyl, cyclohexyl.
- [0021] As used herein, the term “cycloalkyl” means a saturated cyclic hydrocarbon radical, such as, for example, cyclopentyl, cyclohexyl.
- [0022] As used herein, the terminology “(C_n-C_m)” in reference to an organic group, wherein n and m are each integers, indicates that the group may contain from n carbon atoms to m carbon atoms per group.
- [0023] In one aspect, the present invention provides an emulsifiable herbicidal composition comprising:

- a) an agricultural active ingredient of Pinoxaden in an amount from 0.5 to 50 wt.%, based on the total weight of the emulsifiable herbicidal composition;
- b) a solvent selected from a compound of formula (I) in an amount from 1 to 90 wt.%, based on the total weight of the emulsifiable herbicidal composition,



wherein

R¹ and R² are each independently selected from linear or branched C₁-C₁₂ alkyl, C₄-C₁₂ cycloalkyl or aryl; and

R³ is selected from H, linear or branched alkyl, cycloalkyl or a -C(=O)R⁴ group, with R⁴ being selected from a linear or branched alkyl or cycloalkyl.

- [0024] By virtue of the green solvents, the emulsifiable herbicidal compositions comprising the same eliminate the CMR risk as tetrahydrofurfuryl alcohol. Meanwhile, the emulsifiable herbicidal compositions as provided in the present invention have better decomposition inhibition performance and better low temperature stability.
- [0025] In one embodiment of the present invention, the emulsifiable herbicidal composition can be an emulsifiable concentrate, or an oil dispersible suspension.
- [0026] As used herein, an emulsifiable concentrate refers to compositions which form an oil-in-water emulsion upon mixing with water (e.g. in a weight ratio of 1 part concentrate to 99 parts water). The emulsion usually arises spontaneously. The resulting emulsion may have an average droplet size of more than 0.1 μm , preferably more than 0.5 μm , in particular more than 0.8 μm , and most preferred more than 1.1 μm . The resulting emulsion may have an average droplet size of up to 30 μm , preferably up to 10 μm , in particular up to 5 μm . The average droplet size may be determined by laser diffraction, e.g. with a Malvern Mastersizer 3000. The emulsifiable concentrate is preferably present as a homogeneous solution. It is usually virtually free from dispersed particles.
- [0027] As used herein, oil dispersible suspension is a formulation prepared by dispersing solid active ingredients in oil. The oil can be at least one selected from the group consisting of one vegetable or mineral or paraffin oil.
- [0028] Suitable vegetable oils are generally known and commercially available. The term vegetable oils is to be understood as including, for example, oils from oleaginous plant species, such as soya bean oil, rapeseed oil, maize germ oil, maize kernel oil, sunflower oil, cottonseed oil, linseed oil, coconut oil, palm oil, thistle oil, walnut oil, arachis oil, olive oil or castor oil, colza oil, in particular soya bean oil, rapeseed oil, maize germ oil or sunflower oil and mixtures thereof. The vegetable oils (triglycerides) are preferably esters of C_{10} - C_{22} -, preferably C_{12} - C_{20} -, fatty acids of glycerol. The C_{10} - C_{22} -fatty acid esters of glycerol are, for example, esters of unsaturated or saturated C_{12} - C_{20} -fatty acids, in particular those having an even number of carbon atoms, for example erucic acid, lauric acid, palmitic acid, and in particular C_{18} -fatty acids, such as stearic acid, oleic acid, linoleic acid or linolenic acid.
- [0029] Suitable mineral oils are various commercially available distillate fractions of mineral oil (petroleum). Preference is given to mixtures of open-chain C_{14} - C_{30} -hydrocarbons, cyclic hydrocarbons (naphthenes) and aromatic hydrocarbons.

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The hydrocarbons can be either straight-chain or branched. Particular preference is given to mixtures having an aromatic portion of less than 8% by weight. Very particular preference is given to mixtures having an aromatic portion of less than 4% by weight.

[0030] Suitable paraffin oils are straight-chain and branched C₁₄-C₃₀-hydrocarbons. Paraffin oils are also known as base oil or white oil and are commercially available, for example, as Bayol® 85 (Exxon Mobil, Machelen, Belgium), Marcol® 82 (Exxon Mobil, Machelen, Belgium), BAR 0020 (RA.M.oil S.p.A., Naples, Italy), Pionier 0032-20 (Hansen & Rosenthal K G, Hamburg, Germany) or, for example, Kristol M14 (Carless, Surrey, England).

[0031] Active ingredient

[0032] The emulsifiable herbicidal composition of the present invention comprises an agricultural active ingredient of Pinoxaden in an amount from 0.5 to 50 wt.%, preferably 1 to 30 wt.%, most preferably 5 to 20 wt.%, based on the total weight of the emulsifiable herbicidal composition.

[0033] In one embodiment of the present invention, the emulsifiable herbicidal composition can further comprise one or more active ingredients that are compatible with Pinoxaden.

[0034] "Compatible" means in this context that the herbicide combination is chemically stable and exhibits neither antagonism nor increased phototoxicity in respect of the useful plants. Such herbicides are preferably selected from the groups of the sulfonylureas, for example triasulfuron, tribenuron, metsulfuron, thifensulfuron, flupyrsulfuron, chlorsulfuron, prosulfuron, amidosulfuron, mesosulfuron, sulfosulfuron and tritosulfuron, aryloxyphenoxypropionates and heteroaryloxyphenoxypropionates such as clodinafop-propargyl, fenoxaprop-P-ethyl, diclofop-methyl and cyhalofop-butyl, triazolopyrimidines such as florasulam, metosulam and flumetsulam, arylcarboxylic acids, preferably dicamba and clopyralid, also aryloxycarboxylic acids, preferably esters of 2,4-D, 2,4-DP, mecoprop, mecoprop-P, MCPA, MCPB, dichlorprop-P and fluroxypyr, cyclohexanedione oximes such as tralkoxydim, thiocarbamates such as triallate and prosulfocarb, hydroxybenzonitriles such as bromoxynil, bromoxynil octanoate, ioxynil and ioxynil octanoate, dinitroanilines such as pendimethalin and trifluralin, and also pyridinecarboxamides such as diflufenican.

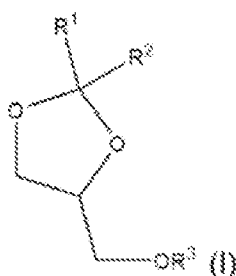
[0035] In one embodiment of the present invention, the emulsifiable herbicidal composition can further comprise one or more active ingredients in an amount from 0.1 to 50 wt.%, preferably 0.5 to 30 wt.%, most preferably 1 to 20 wt.%,

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based on the total weight of the emulsifiable herbicidal composition. The weight ratio of Pinoxaden to other active ingredients is between 1:50 to 50:1, preferably 1:20 to 20:1.

[0036] Solvent

[0037] In various embodiment of the present invention, the emulsifiable herbicidal composition comprises a solvent selected from a compound of formula (I) in an amount from 1 to 90 wt.%, preferably 5 to 60 wt.%, more preferably 15 to 40 wt.%, based on the total weight of the emulsifiable herbicidal composition,



wherein

R^1 and R^2 are each independently selected from linear or branched C_1 - C_{12} alkyl, C_4 - C_{12} cycloalkyl or aryl; and

R^3 is selected from H, linear or branched alkyl, cycloalkyl or a $-C(=O)R^4$ group, with R^4 being selected from a linear or branched alkyl or cycloalkyl.

[0038] In one embodiment of the present invention, R^1 and R^2 are each independently selected from methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, tert-butyl, n-pentyl, cyclopentyl, cyclohexyl or phenyl.

[0039] In another embodiment of the present invention, R^3 is selected from H or $-C(=O)R^4$ group, with R^4 being selected from methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl or tert-butyl.

[0040] In still another embodiment of the present invention, R^1 and R^2 are methyl and R^3 is H.

[0041] In yet another embodiment of the present invention, R^1 is methyl, R^2 is isobutyl and R^3 is H.

[0042] In yet still another embodiment of the present invention, R^1 is methyl, R^2 is phenyl and R^3 is H.

[0043] In yet still another embodiment of the present invention, R^1 and R^2 are methyl, and R^3 is a $-C(=O)R^4$ group, with R^4 being methyl.

- [0044] In some embodiments of the present invention, the emulsifiable herbicidal composition can further comprise one or more other solvents. Preferably, such other solvents include but not limited to dimethylsulphoxide (DMSO), cyclohexanone (CYC), dimethylformamide (DMF), N-methyl pyrrolidinone (NMP), acetophenone, and aromatic solvents, such as toluene, xylene, light aromatic solvent naphtha (C8 to C10) sold under the trade name of Solvesso™ 100 and heavy aromatic solvent (C10 and C10 to C13) sold under the trade name of Solvesso™ 150 and Solvesso™ 200.
- [0045] Other Component
- [0046] In some embodiment of the present invention, the emulsifiable herbicidal composition can further comprise safeners, preference being given to cloquintocet-mexyl, mefenpyr-diethyl or isoxadifen-ethyl and derivatives thereof, such as the corresponding acid and salts. Such safeners are described, for example, in The Pesticide Manual, 12th Edition, BCPC, and in DE-A-43 31 448, which are incorporated herein by reference in its entirety.
- [0047] In some embodiment of the present invention, the emulsifiable herbicidal composition can further comprise emulsifiers, preferably, the emulsifiers are selected from the group consisting of non-ionic surfactant and anionic surfactant.
- [0048] Suitable non-ionic surfactants or dispersing aids are all substances of this type which can customarily be employed in agrochemical agents. Preferably, polyethylene oxide-polypropylene oxide block copolymers, polyethylene glycol ethers of linear alcohols, reaction products of fatty acids with ethylene oxide and/or propylene oxide, furthermore polyvinyl alcohol, polyvinylpyrrolidone, copolymers of polyvinyl alcohol and polyvinylpyrrolidone, and copolymers of (meth)acrylic acid and (meth)-acrylic acid esters, furthermore alkyl alkoxylates and alkylaryl alkoxylates, which can be optionally phosphated and optionally neutralized with bases, where sorbitol ethoxylates may be mentioned by way of example, and polyoxyalkylenamine derivatives are employed.
- [0049] Possible anionic surfactants are all substances of this type which can customarily be employed in agrochemical agents. Alkali metal and alkaline earth metal salts of alkylsulphonic acids or alkylarylsulphonic acids are preferred.
- [0050] A further group of anionic surfactants which can be contemplated in the present invention are salts of polystyrenesulphonic acids, salts of polyvinylsulphonic acids, salts of naphthalenesulphonic acid-formaldehyde condensation products, salts of condensation products of naphthalenesulphonic acid, phenolsulphonic

acid and formaldehyde, and salts of liginosulphonic acid, which are not very soluble in vegetable oil.

[0051] Preferred emulsifiers are ethoxylated nonylphenols, reaction products of alkylphenols with ethylene oxide and/or propylene oxide, ethoxylated arylalkylphenols, furthermore ethoxylated and propoxylated arylalkylphenols, and sulphated or phosphated arylalkyl ethoxylates or -ethoxy-propoxylates, where sorbitan derivatives, such as polyethylene oxide-sorbitan fatty acid esters and sorbitan fatty acid esters, may be mentioned by way of example.

[0052] Adjuvants may also be added to the emulsifiable herbicidal composition according to the present invention. Such adjuvants can include but not limited to, organosilicon surfactants, mineral oil derivatives with and without surfactants, vegetable oil derivatives with and without added surfactant, fish oils and other oils of animal nature and alkyl derivatives thereof with and without surfactants, naturally occurring higher saturated and mono- or poly-unsaturated fatty acids, preferably having from 8 to 28 carbon atoms, and alkyl ester derivatives thereof, organic acids containing an aromatic ring system and one or more carboxylic acid radicals, as well as alkyl derivatives thereof. Mixtures of individual adjuvants with one another and in combination with organic solvents can result in a further enhancement of action.

[0053] The preparation of the emulsifiable herbicidal composition according to the present invention is carried out substantially in accordance with the known customary method of dissolving or dispersing Pinoxaden and optionally herbicides in the solvents as described herein, and then adding a customary emulsifier. The mixture so obtained is stirred or grinded until the composition has been formed.

[0054] Dilution of the emulsifiable herbicidal composition

[0055] In another aspect of the present invention, it is provided a dilution of the emulsifiable herbicidal composition. The dilution can be prepared by diluting the emulsifiable herbicidal composition with aqueous medium for 10 to 2000 times, notably executed by end users, like farmers.

[0056] The "aqueous medium" is particularly selected from water. In some embodiments, extra organic solvents, like ethanol, can be added.

[0057] During the diluting process, other pesticide formulations, fertilizers, and other tank mixing adjuvants can be added based on the need.

[0058] In still another aspect of the present invention, it is provided a method of controlling the growth of unwanted plants, comprising a step of applying to the

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plants or to the locus of unwanted plant an effective amount of a dilution as described herein.

[0059] In one embodiment of the present invention, the dilution can be sprayed to the plants or to the locus of unwanted plant.

[0060] In yet still another aspect of the present invention, it is provided a use of a compound of formula (I) in inhibiting the decomposition of Pinoxaden in emulsifiable herbicidal compositions.

[0061] In yet still another aspect of the present invention, it is provided a use of a compound of formula (I) in preparing emulsifiable herbicidal compositions comprising an agricultural active ingredient of Pinoxaden.

[0062] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

EXAMPLE

[0063] Materials

- Pinoxaden: active ingredient, 96% active content;
- Cloquintocet-mexyl: 97% active content, herbicide safener available from Lier Chemical;
- Rhodacal 60BE-C: an anionic emulsifier from Solvay;
- Soprophor 796P: a non-ionic emulsifier available from Solvay;
- Augeo SL191: solvent, 1, 1,2-Isopropylideneglycerol, available from Solvay;
- Augeo Clean Plus: solvent, (2-isobutyl-2-methyl-1,3-dioxolan-4-yl)methanol, available from Solvay;
- S150: aromatic solvent available from Jiangsu Hualun.

[0064] Example 1: decomposition rate of the emulsifiable herbicidal compositions

[0065] 1. The preparation of the emulsifiable herbicidal compositions

[0066] The emulsifiable herbicidal compositions were prepared by mixing Pinoxaden, Cloquintocet-mexyl, solvent and S150 successively, and then stirring to a homogeneous and transparent solution at room temperature. Afterwards, Rhodacal 60BE-C and Soprophor 796P were added and stirred until a uniform mixture was obtained.

[0067] 2. Decomposition evaluation of the emulsifiable herbicidal compositions

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[0068] The compositions as prepared above were left standing at 54 °C and room temperature (RT) for two weeks separately. Then the content of the active ingredient (AI content) was determined by HPLC, and the decomposition rate was calculated according to the formula below:

$$\text{Decomposition rate (\%)} = \frac{\text{AI content at RT\%} - \text{AI content at 54 } ^\circ\text{C\%}}{\text{AI content at RT\%}} * 100\%$$

[0069] The composition rates were shown in the table 1. In the following tables, "S" refers to the samples representing the present invention, and "CS" refers to Comparative Samples, and each components were weighted as parts by weight (wt.%).

Table 1: decomposition rate of the emulsifiable herbicidal compositions

Composition (Parts by weight, wt.%)	S1	S8	CS1	CS2	CS3	CS4	CS5	CS6	CS7	CS8
Pinoxaden	5.3									
Cloquintocet- mexyl 97%	1.3									
S150	58.4									
Rhodacal 60BE-C	4									
Soprophor 796P	6									
Solvent (25 wt. %)	Augeo SL191	Augeo Clean Plus	Cyclohex anone	Propylene carbonate	Pheneth yl alcohol	Diethyleneg lycolmonob utylether	Dipropylene Glycol Methyl Ether	Gamma- Butyrolac tone	2-methyl- 2,4- pentanedi ol	Tetrahyd rofuranyl alcohol
AI content at 54 °C (wt.%)	4.9	5.04	3.12	3.85	4.13	3.85	4.04	3.4	4.94	4.41
AI content at RT(wt.%)	5.04	5.30	4.63	4.52	4.69	4.71	4.72	4.58	5.13	4.52
Decomposition rate(%)	2.78	4.91	32.61	14.82	11.94	18.26	14.41	25.76	3.7	2.43

Table 1 continued

Composition (Parts by weight, wt.%)	S2	S3
Pinoxaden	5.3	
Cloquintocet-mexyl (97%)	1.3	
Rhodacal 60BE-C	4	
Soprophor 796P	6	
Augeo SL191	25	83.4
1,2-Propanediol	58.4	0
Al content at 54 °C (wt.%)	5.15	5.04
Al content RT (wt.%)	5.16	5.05
Decomposition-rate (%)	0.19	0.2

- [0070] It was shown that Augeo SL191 could inhibit the decomposition of Pinoxaden in the emulsifiable herbicidal compositions according to the invention, which is comparable to the benchmark CS8, but eliminate the concern of CMR at the same time.
- [0071] EXAMPLE 2: solubility and stability of the emulsifiable herbicidal compositions
- [0072] The samples were prepared by mixing Pinoxaden (Al), Cloquintocet-mexyl, Solvent and S150 successively, and then stirring to a homogeneous and transparent solution at room temperature. After that, the solutions were heated at 60 °C for 15 minutes. The solutions were observed in visual, before and after heating, to check whether there were unsolved solids. "Good" means no visible solids observed in the solutions, "partially dissolved" means some visible solids were observed in the solutions.
- [0073] The heated solutions were left standing at 0 °C for 7 days, then the solutions were observed in visual to check whether crystals were formed from the solutions. Afterwards, trace Pinoxaden was added to the solutions as seed crystal, then solutions were observed in visual 7 days after adding the seed crystal to check whether there were crystals formed from the solutions. "Good" means no visible crystals observed in the solutions, "crystal" means some visible Crystals were observed in the solutions.

Table 2: low temperature stability of the emulsifiable herbicidal compositions

	S4	S5	S6	S7	CS9	CS10	CS11	CS12	CS13
AI(96%)	23.40%	23.40%	23.40%	23.40%	23.40%	23.40%	23.40%	23.40%	23.40%
Augeo SL191	22.20%	33.30%	44.40%	55.50%					
2-methyl-2,4-pentanediol					22.20%	33.30%	44.40%	55.50%	
S150 LN	54.40%	43.30%	32.20%	21.10%	54.40%	43.30%	32.20%	21.10%	76.60%
RT, Solubility	Good	Good	Good	Good	Partially dissovled	Partially dissovled	Partially dissovled	Partially dissovled	Partially dissovled
60C, Solubility	Good	Good	Good	Good	Good	Good	Good	Good	Partially dissovled
Stability, 0C 7d	Good	Good	Good	Good	Crystal	Good	Good	Good	N/A
Seeding, 0C 7d	Good	Good	Good	Good	N/A	Crystal	Crystal	Crystal	N/A

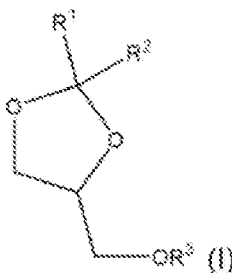
Table 2 continued

	S9	S10	S11	S12
AI(96%)	23.40%	23.40%	23.40%	23.40%
Augeo Clean plus	22.20%	33.30%	44.40%	55.50%
S150 LN	54.40%	43.30%	32.20%	21.10%
RT, Solubility	Good	Good	Good	Good
60C, Solubility	Good	Good	Good	Good
Stability, 0C 7d	Good	Good	Good	Good
Seeding, 0C 7d	Good	Good	Good	Good

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CLAIMS

1. An emulsifiable herbicidal composition comprising:
 - a) an agricultural active ingredient of Pinoxaden in an amount from 0.5 to 50 wt.%, based on the total weight of the emulsifiable herbicidal composition;
 - b) a solvent selected from a compound of formula (I) in an amount from 1 to 90 wt.%, based on the total weight of the emulsifiable herbicidal composition,



wherein

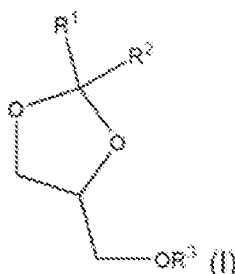
- R^1 and R^2 are each independently selected from linear or branched C_1 - C_{12} alkyl, C_4 - C_{12} cycloalkyl or aryl; and
- R^3 is selected from H, linear or branched alkyl, cycloalkyl or a $-C(=O)R^4$ group, with R^4 being selected from a linear or branched alkyl or cycloalkyl.
2. The emulsifiable herbicidal composition according to claim 1, wherein R^1 and R^2 are each independently selected from methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl, tert-butyl, n-pentyl, cyclopentyl, cyclohexyl or phenyl.
 3. The emulsifiable herbicidal composition according to claim 1 or 2, wherein R^3 is selected from H or $-C(=O)R^4$ group, with R^4 being selected from methyl, ethyl, isopropyl, n-propyl, isobutyl, n-butyl or tert-butyl.
 4. The emulsifiable herbicidal composition according to claim 1, wherein R^1 and R^2 are methyl and R^3 is H.
 5. The emulsifiable herbicidal composition according to claim 1, wherein R^1 is methyl, R^2 is isobutyl and R^3 is H.

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6. The emulsifiable herbicidal composition according to claim 1, wherein R¹ is methyl, R² is phenyl and R³ is H.
7. The emulsifiable herbicidal composition according to anyone claim 1, wherein R¹ and R² are methyl, and R³ is a $-C(=O)R^4$ group, with R⁴ being methyl.
8. The emulsifiable herbicidal composition according to anyone of claims 1 to 7, wherein the emulsifiable herbicidal composition further comprises one or more emulsifiers selected from the group consisting of non-ionic surfactant and anionic surfactant.
9. The emulsifiable herbicidal composition according to any one of claims 1 to 8, wherein the emulsifiable herbicidal composition further comprises one or more herbicides selected from the group consisting of triasulfuron, tribenuron, metsulfuron, thifensulfuron, flupyrsulfuron, chlorsulfuron, prosulfuron, amidosulfuron, mesosulfuron, sulfosulfuron, tritosulfuron, clodinafop-propargyl, fenoxaprop-P-ethyl, diclofop-methyl, cyhalofop-butyl, florasulam, metosulam, flumetsulam, dicamba, clopyralid, an ester of 2,4-D, 2,4-DP, mecoprop, mecoprop-P, MCPA, MCPB, dichlorprop-P, fluroxypyr, tralkoxydim, triallate, prosulfocarb, bromoxynil, bromoxynil octanoate, ioxynil, ioxynil octanoate, pendimethalin, trifluralin, and diflufenican.
10. The emulsifiable herbicidal composition according to anyone of claims 1 to 9, wherein the emulsifiable herbicidal composition is an emulsifiable concentrate or an oil dispersible suspension.
11. A dilution of the emulsifiable herbicidal composition according to anyone of claims 1 to 10, prepared by diluting the emulsifiable herbicidal composition with aqueous medium for 10 to 2000 times.
12. A method of controlling the growth of unwanted plants, comprising a step of applying to the plants or to the locus of unwanted plant an effective amount of the dilution according to claim 11.

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13. Use of a compound of formula (I) in inhibiting the decomposition of Pinoxaden in emulsifiable herbicidal compositions,

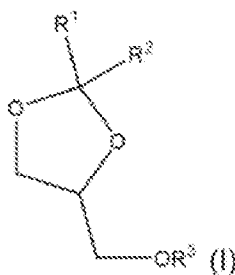


wherein

R¹ and R² are each independently selected from linear or branched C₁-C₁₂ alkyl, C₄-C₁₂ cycloalkyl or aryl; and

R³ is selected from H, linear or branched alkyl, cycloalkyl or a -C(=O)R⁴ group, with R⁴ being selected from a linear or branched alkyl or cycloalkyl.

14. Use of a compound of formula (I) as a solvent for preparing emulsifiable herbicidal compositions comprising an agricultural active ingredient of Pinoxaden,



wherein

R¹ and R² are each independently selected from linear or branched C₁-C₁₂ alkyl, C₄-C₁₂ cycloalkyl or aryl; and

R³ is selected from H, linear or branched alkyl, cycloalkyl or a -C(=O)R⁴ group, with R⁴ being selected from a linear or branched alkyl or cycloalkyl.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/107239

A. CLASSIFICATION OF SUBJECT MATTER

A01N 25/04(2006.01)i; A01N 43/90(2006.01)i; A01P 13/00(2006.01)i

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 25/-, A01N 43/-, A01P 13/-

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)

CNPAT, CNKI, EPODOC, WPI, STN: RHODIA OPERATIONS, Pinoxaden, emulsifiable, emulsion, herbicidal, composition, dispersion, solvent, dioxolane, 243973-20-8

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CN 110402923 A (SHANXI AGRICULTURAL UNIVERSITY) 05 November 2019 (2019-11-05) paragraph 0050, claim 9, abstract	1-14
Y	WO 2014125357 A1 (RHODIA POLIAMIDA E ESPECIALIDADES LTDA) 21 August 2014 (2014-08-21) claims 1, 6	1-14
A	WO 2014152246 A1 (SEGETIS, INC.) 25 September 2014 (2014-09-25) claims 1, 15	1-14



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

08 October 2021

Date of mailing of the international search report

18 October 2021

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2021/107239

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				EP	2967055 A4	31 August 2016
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