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(54) Title: HERBICIDAL COMPOSITION

(57) Abstract: The present invention relates to a herbicidal emulsifiable concentrate composition comprising: (a) 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate; (b) a solvent blend comprising propylene carbonate and one or more other organic solvent(s); and (c) one or more emulsifiers. The present invention further relates to methods of controlling weeds using the herbicidal emulsifiable concentrate.

HERBICIDAL COMPOSITION

The present invention relates to a herbicidal emulsifiable concentrate (EC) composition which comprises 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate as the herbicidally active compound, and to the use of such a composition in controlling weeds in crops of useful plants.

EC compositions are attractive in the agrochemical industry for delivering active ingredients that are soluble in organic solvents. They typically offer good chemical stability, provide high biological activity, are easy to pour and measure and are simple to manufacture. Typically, EC compositions are made by dissolving the active ingredient of interest in the organic solvent (e.g. an oil), along with emulsifying surfactant(s) that ensure spontaneous emulsification of the EC composition when added into water in, for example, a spray tank.

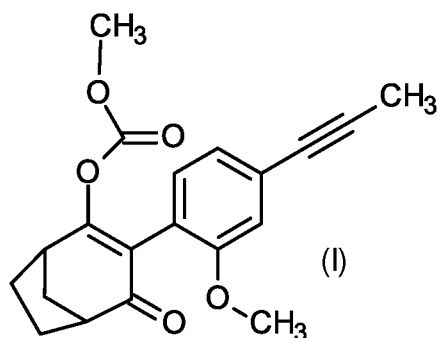
Whilst EC compositions are attractive option for the agrochemical formulator, many pesticides are unfortunately not soluble enough to be supplied economically as EC compositions. In order to try and increase the solubility of a particular active ingredient, the agrochemical formulator will often attempt to combine the organic solvent with one or more polar solvent(s) to form a solvent blend.

3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate (CAS RN 1848207-89-5) is disclosed as a herbicidal compound in WO2015/197468 and exhibits selective herbicidal action against weeds in certain crops such as soybean, especially against grasses such as *Sorghum halepense*, *Digitaria insularis* and *Eleusine indica*. WO2015/197468 teaches that the compounds disclosed therein can be formulated in numerous composition types including, for example, as an EC composition. However, 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate isn't particularly soluble in solvents typically employed in EC composition, such as those referred to generally in WO2015/197468. The present invention is thus based on the finding that the solubility of 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate can be greatly enhanced using a specific solvent blend, to the extent that solubility in the solvent blend is surprisingly greater than that observed with regard to the individual solvent components. This observed solubility synergy advantageously provides for more concentrated EC compositions.

Thus, according to the present invention there is provided an emulsifiable concentrate composition comprising:

- (a) 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate;
- (b) a solvent blend comprising propylene carbonate and one or more organic solvents; and
- (c) one or more emulsifiers.

3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate has the chemical structure shown below:



and is known, for example, from WO2015/197468.

Preferably the emulsifiable concentrate composition of the present invention comprises from 1 to 50 % w/v of 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate, more preferably from 10 to 30 % w/v, and especially from 15 to 25 % w/v.

The solvent blend, in addition to the propylene carbonate, contains one or more organic solvents. Examples of such organic solvents include aromatic hydrocarbons, such as toluene, xylene, cumene, mixtures of aromatic hydrocarbons having a boiling point of from 160°C to 180°C (Solvesso® 100) or from 180°C to 210°C (Solvesso® 150) or from 230°C to 290°C (Solvesso® 200), aliphatic or cycloaliphatic hydrocarbons (Exxsol™ D80, Exxsol™ D100, Exxsol™ D120, Isopar™ H and Isopar™ V), fatty alcohol acetates (Exxate™ 700, Exxate™ 1000), isobornyl acetate, benzyl acetate (eg, Jeffsol® AG 1705, Huntsman Corporation Australia Pty Ltd), lower alkyl esters of dicarboxylic acids such as maleic, fumaric, succinic, glutaric and adipic acid (Solvent DBE), lactic acid ethyl ester (e.g Purasolv® EL), esters of benzoic acid such as benzyl benzoate, methyl benzoate (Polynt S.p.A., Italy), butyl benzoate (e.g Jeffsol® AG 1700) and dipropylene glycol dibenzoate, as well as lower alkyl esters of higher fatty acids such as C₈-C₁₀fatty acid methyl esters and C₁₆-C₁₈fatty acid methyl esters, benzyl alcohol, methyl 5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv® Polarclean) and ketones such as cyclohexanone, acetophenone, methyl-n-pentyl ketone. Solvesso™ 200 (or the naphthalene-depleted version Solvesso™ 200ND) is particularly

preferred, as this exhibits striking solubility synergy of 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate with the propylene carbonate.

Whilst the solvent blend can contain one or more of these organic solvents, it is preferred that the solvent blend consists of propylene carbonate and just one additional organic solvent. In a more preferred embodiment of the present invention, the one organic solvent is selected from the group consisting of methyl benzoate, acetophenone, benzyl benzoate, benzyl acetate (eg, Jeffsol® AG 1705), butyl benzoate (e.g Jeffsol® AG 1700), lactic acid ethyl ester (Purasolv® EL), benzyl alcohol and mixtures of aromatic hydrocarbons having a boiling point of from 230 to 290°C (Solvesso® 200). In a more preferred embodiment the one organic solvent selected from the group consisting of methyl benzoate, acetophenone, benzyl benzoate, benzyl alcohol, benzyl acetate (eg, Jeffsol® AG 1705), butyl benzoate (e.g Jeffsol® AG 1700) and mixtures of aromatic hydrocarbons having a boiling point of from 230 to 290°C (Solvesso® 200). In a more preferred embodiment the one organic solvent is a mixture of aromatic hydrocarbons having a boiling point of from 230 to 290°C (Solvesso® 200).

In one embodiment of the present invention, the ratio of propylene carbonate : organic solvent is 100:1 to 1:100 w/v, more preferably from 5:1 to 1:5, more preferably from 1:3 to 3:1. In one embodiment of the present invention the herbicidal emulsifiable concentrate composition comprises from 50% to 70% w/v solvent blend.

From the data presented in Figure 1 and Figure 2 below it can be seen that solubility synergy observed is between the propylene carbonate and many organic solvents, which surprisingly increases the solubility greater than the of the individual solvents alone. This solubility synergy provides significant benefits, including the provision of a solvent blend that make easier-to-emulsify formulations and maximises the active ingredient loading in the EC composition, whilst providing more low-temperature robustness. The synergy is observed at both 5°C (Figure 1) and 25°C (Figure 2). Positive synergy is especially apparent for propylene carbonate blends with benzyl benzoate, Jeffsol® AG1700, Jeffsol® AG1705 and very significant for Solvesso® 200ND. Of particular note is the solubility boost observed with propylene carbonate / Solvesso® 200ND. Solvesso® 200ND is often conveniently used as a solvent in EC compositions but was virtually discounted as part of a high loading formulation for 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate due to the relatively low solubility of the herbicide in Solvesso® 200ND alone. However, solvent blends with propylene carbonate have successfully overcome this drawback.

For the one or more emulsifier component of the composition it is possible to use the emulsifiers customarily used in connection with ECs. The exact nature of the emulsifier(s) is not germane to the present invention and the skilled person is well aware of many emulsifying surfactant systems which enable the forming of an oil in water emulsion when the emulsifiable concentrate is diluted with an aqueous solution. Such an emulsifying surfactant system may comprise one or more emulsifying surfactants. The emulsifying surfactant(s) may be non-ionic, anionic, cationic or zwitterionic. Examples of particular suitable surfactants include, but are not limited to, alkyl polyglycosides, polyalkylene oxide block copolymers and polyaryl-phenyl ether phosphates. Alkyl polyglycosides include Agnique PG ("APG") 8107 (Cognis Corporation, Cincinnati, Ohio, USA) (an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and has an average degree of polymerization of 1.7), Agnique PG 9116 (Cognis Corporation, Cincinnati, Ohio, USA) (a 20 alkyl polyglycoside in which the alkyl group contains 9 to 11 carbon atoms and has an average degree of polymerization of 1.6) and Agnique PG 8105 (Cognis Corporation, Cincinnati, Ohio, USA) (an alkyl polyglycoside in which the alkyl group contains 8 to 10 carbon atoms and has an average degree of polymerization of 1.5). Polyalkylene oxide block copolymers can be di- and tri-block copolymers, such as ABA or BAB block copolymer or BA block copolymers. Examples include the Genapol PF series (Clariant), the Pluronic series (BASF), the Synperonic PE series (Uniqema), and the Toximul series (Stepan Chemical Co.). A group of ethylene oxide/propylene oxide block copolymers which may be used in the compositions of this invention are butyl-based poly(oxypropylene)/poly(oxyethylene)block copolymers having an average molecular weight in the range of 2400 to 3500, for example Toximul 8320, Stepan Chemical Co.). Suitable examples include Pluronic L10, Pluronic L44, Pluronic L63, Pluronic L64, Pluronic L84, Pluronic P104, Pluronic P105, Step-Flow 26, Toximul 8323 and Toximul 8320. Polyaryl-phenyl ether phosphates include ethoxylated tristyrylphenol phosphates such as Soprophor 35 3D33 (Rhodia), Soprophor 3D33 LN (Rhodia), Soprophor BSU (Rhodia), Emulsogen 57 (Clariant), Agnique PE TSP-16A (BASF), Agrhospec 7822 (Rhodia), Dispersogen TP 160 (Clariant), Stepfac TP 160 (Stepan), Stepfac TSP-PE (Stepan). The degree of ethoxylation of the polyaryl-phenyl ether phosphates for this purpose is preferably between 8 and 20, more preferably between 14 and 18. Preferred examples that may be mentioned in the context of the composition of the present invention are castor oil ethoxylates e.g Emulsogen EL 360 (Clariant) and especially low ion quality castor oil ethoxylates such as Tergitol™ ECO-30 HP (Dow) or Alkamuls EL-620/LI (Solvay) with a tristyryl phenol ethoxylates (such as Soprophor BSU), mixtures thereof in combination with anionic surface-active compounds such as the calcium salt of dodecyl-benzenesulfonic acid or the sodium salt of dioctylsulfosuccinic acid (NANSA® EVM).

Preferably from 0.5 to 50 % w/v of the one or more emulsifiers are present in the EC composition of the invention. A content of from 2 to 30 % w/v, especially from 2 to 10 % w/v, is especially preferred.

5 The compositions according to the invention may comprise, in addition to 2-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate, one or more further herbicides that are compatible with the EC formulation. "Compatible" means in this context that the herbicide combination is chemically stable and physically stable in the EC formulation. The EC compositions according to the invention can also include herbicide safeners, preference being given to cloquintocet-mexyl, isoxadifen-ethyl, mefenpyr-diethyl
10 and metcamifen or and derivatives thereof, such as the corresponding acid and salts.

The preparation of the ECs according to the invention is carried out substantially in accordance with the known customary method of dissolving the herbicide in the solvent blend and then adding a customary emulsifier. The mixture so obtained is stirred until a clear solution has been formed.

15 Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ formulations diluted with water. The end user may also employ tank-mix adjuvants such as ammonium sulfate (e.g 2.5%) and crop oil concentrate 1.0%. Other commercially-available adjuvant products which may be tank-mixed to yield a spray formulation with the composition of the present invention include Adigor® (Syngenta – a
20 methylated rapeseed oil based adjuvant), Aureo (Bayer AG – soybean oil methyl ester), HASTEN™ (Victorian Chemical Co. Pty. Ltd. - blend of an esterified vegetable oil and non-ionic surfactants), OCHIMA® (Syngenta - alkyl ester of phosphoric acid (EC formulation)), LEDNA™ (Polaquimia - EC formulation comprising a methyl ester of soybean oil), Atplus® 463 (CRODA Europe Limited - 60% paraffin oil with surfactant blend), Actirob® B (Bayer AG -
25 rapeseed oil methyl ester (esterified vegetable oil)), Destiny® HC (Winfield Solutions LLC - methylated soybean oil), DYNE-AMIC® (HELENA - blend of (methylated) vegetable oil and organosilicone-based nonionic surfactants), FS Optique™ (GROWMARK, Inc - methyl ester of canola oil) and tris(2-ethylhexyl) phosphate (TEHP, CAS no. 78-42-2. Synergen™ TEHP (Clariant GmbH), Disflamoll® TOF (Lanxess)) and Marlox RT64 (Sasol - Fatty Alcohol
30 Alkoxylate).

The compositions according to the invention may also be tank-mixed with other agrochemical products, especially one or more further herbicide products, especially glufosinate or glufosinate-P (L-glufosinate).

Example 1

Various samples are prepared such that 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate is present in the solvent (or solvent blend) at a concentration of 300g/L. The samples are then incubated with gentle agitation in storage ovens for two weeks at 5°C and 25°C. After this time, HPLC analysis is performed on the supernatant of each sample to yield a dissolved concentration of the 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate in the solvent or solvent blend (%w/v). The results observed are shown in Table 1 and 2 below and summarised in Figure 1 and Figure 2. As can be seen, the solubility 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate is unexpectedly improved when propylene carbonate / organic solvent blends are utilised as opposed to 100% propylene carbonate (0% solvent data point) v. 100% organic solvent (100% solvent data point).

Table 1. Solubility results 5°C - Solubility (% w/v)

% Propylene Carbonate	100	75	50	25	0
% Organic Solvent	0	25	50	75	100
Benzyl Alcohol	11	16	17	20	18
Jeffsol AG 1700	11	16	17	12	6
Jeffsol AG 1705	11	15	17	18	15
Methyl Benzoate	11	16	18	20	16
Purasolv EL	11	14	14	9	6
Rhodiasolv Polarclean	11	12	13	12	9
Solvesso 200 ND	11	17	17	14	7

Table 2 Solubility results 25°C - Solubility (% w/v)

% Propylene Carbonate	100	75	50	25	0
% Organic solvent	0	25	50	75	100
Acetophenone	21	27	29	29	29
Benzyl Alcohol	21	26	30	29	29
Benzyl Benzoate	21	26	28	23	18
Jeffsol AG 1700	21	24	25	20	11
Jeffsol AG 1705	21	27	30	29	23
Methyl Benzoate	21	28	29	29	27
Purasolv EL	21	23	20	17	13
Rhodiasolv Polarclean	21	23	21	21	19
Solvesso 200 ND	21	28	30	24	12

Claims

1. A herbicidal emulsifiable concentrate composition comprising:
 - 5 (a) 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate;
 - (b) a solvent blend comprising propylene carbonate and one or more other organic solvent(s); and
 - (c) one or more emulsifiers.
- 10 2. A herbicidal emulsifiable concentrate composition according to claim 1, which comprises from 10% to 30% w/v 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate.
- 15 3. A herbicidal emulsifiable concentrate composition according to claim 2, which comprises from 15% to 25% w/v 3-[2-methoxy-4-(1-propyn-1-yl)phenyl]-4-oxobicyclo[3.2.1]oct-2-en-2-yl methyl carbonate.
- 20 4. A herbicidal emulsifiable concentrate composition according to any one of the previous claims, wherein the solvent blend consists of propylene carbonate and one other organic solvent.
5. A herbicidal emulsifiable concentrate composition according to claim 4, wherein the ratio of propylene carbonate : organic solvent is from 100:1 to 1:100 w/v.
- 25 6. A herbicidal emulsifiable concentrate composition according to claim 5, wherein the ratio of propylene carbonate : organic solvent is from 5:1 to 1:5.
7. A herbicidal emulsifiable concentrate composition according to any one of the previous claims, which comprises from 50% to 70% solvent blend.
- 30 8. A herbicidal emulsifiable concentrate composition according to any one of the previous claims, which comprises 5% to 20% of the one or more emulsifiers.
- 35 9. A method of controlling weeds at a locus, said method comprising diluting the herbicidal emulsifiable concentrate composition according to any one of the previous with water in a spray tank and applying the diluted composition to the locus.

10. A method according to claim 9, wherein a spray-tank claims, wherein a tank-mix adjuvant is included in the spray tank.
- 5 11. A method according to claim 10, wherein the tank-mix adjuvant is an alkyl ester of phosphoric acid.
12. A method according any one of claims 9 to 11, wherein another herbicide product in included in the spray tank.
- 10 13. A method according to claim 12, wherein the herbicide product is a glufosinate-containing product.

FIGURE 1

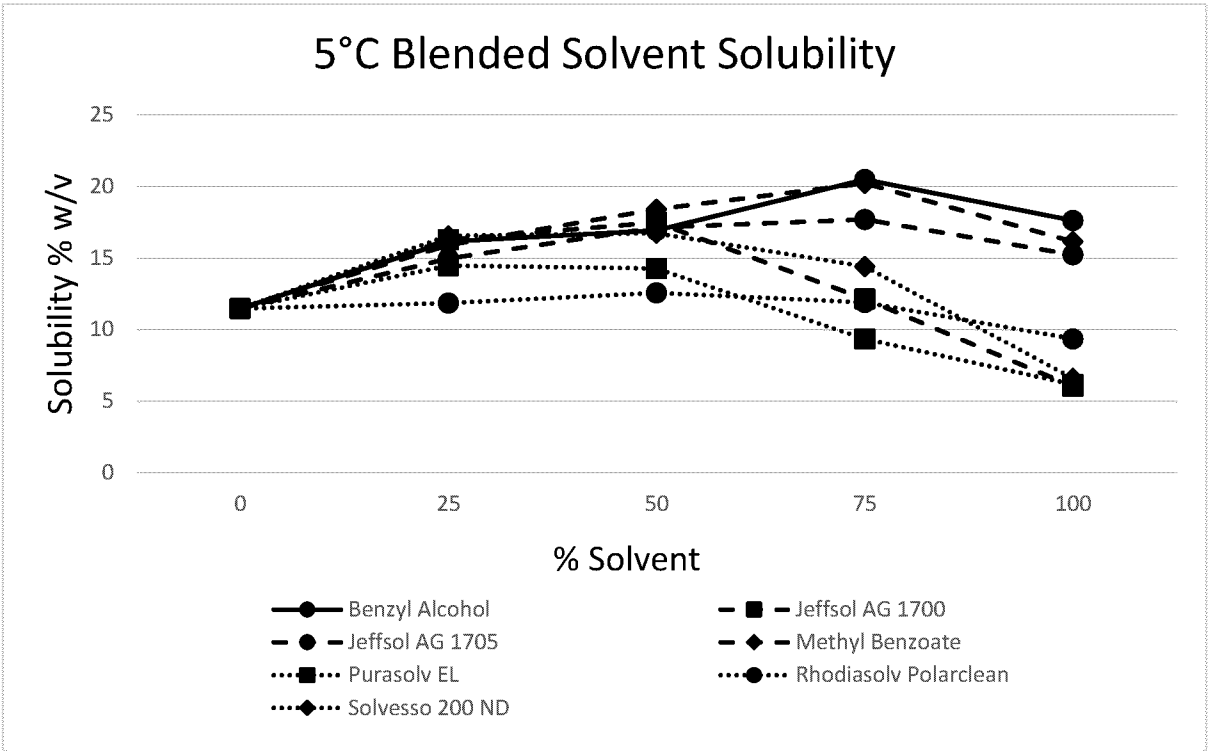
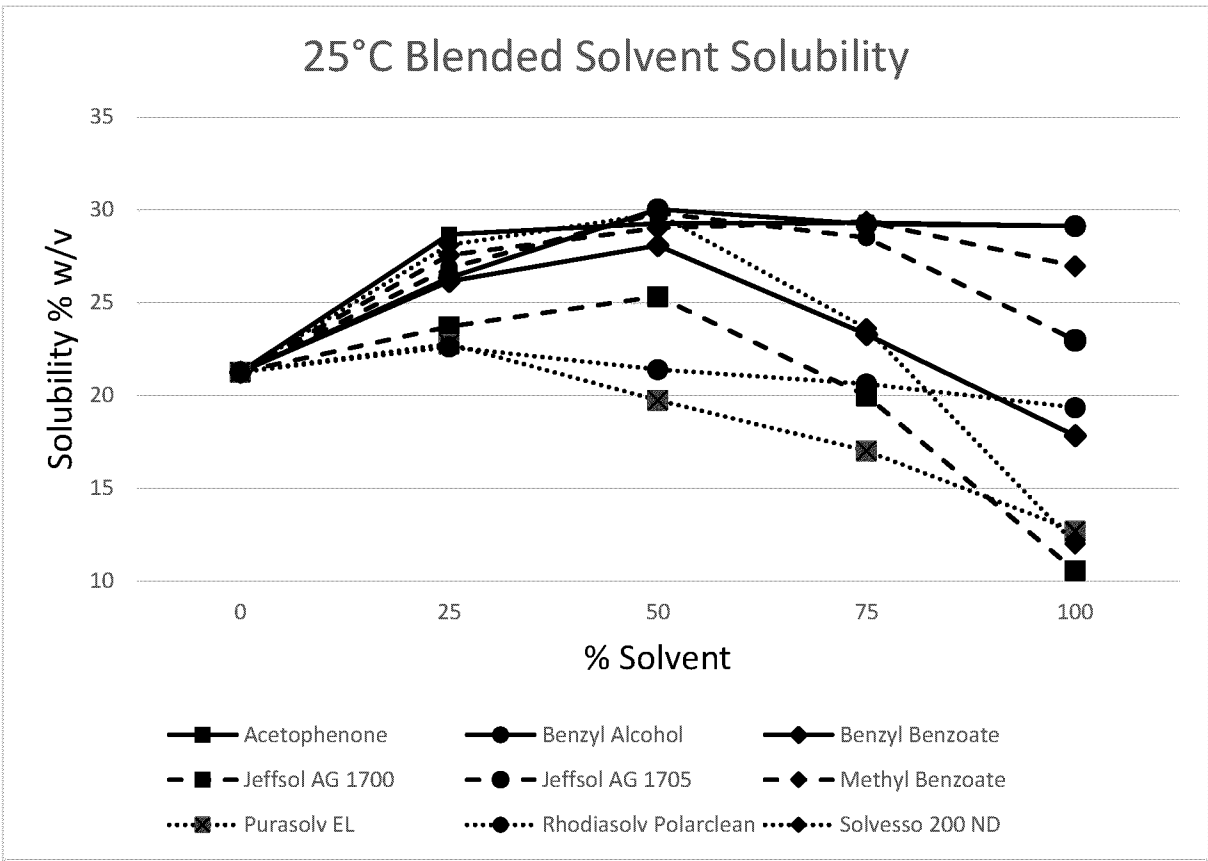


FIGURE 2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/075036

A. CLASSIFICATION OF SUBJECT MATTER INV. A01N47/20 A01P13/00 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, BIOSIS		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/197468 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 30 December 2015 (2015-12-30) cited in the application claims 1-15 page 68, lines 1-22 page 74, lines 3-6 -----	1 - 13
A	WO 2023/280703 A1 (SYNGENTA CROP PROTECTION AG [CH]) 12 January 2023 (2023-01-12) claims 1-15 -----	1 - 13
☐ 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 24 October 2024		Date of mailing of the international search report 31/10/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Marie, Gérald

INTERNATIONAL SEARCH REPORT

Information on patent family members

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