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(54) Title: PYRASULFOTOLE AND PICOLINAFEN COMPOSITION

(57) Abstract: A herbicide composition comprising a synergistically effective amount of pyrasulfotole and picolinafen is provided. Also provided are combinations of the herbicide composition with other herbicidally active compounds. Also provided is a method of controlling or suppressing broad-leaved weeds including wild radish (Raphanus raphanistrum) in a field by sequentially or simultaneously applying pyrasulfotole and picolinafen to that field.

PYRASULFOTOLE AND PICOLINAFEN COMPOSITION

FIELD OF THE INVENTION

[0001] This invention relates to a herbicidal composition which includes 2,5-dimethyl-4-[2-methylsulfonyl-4-(trifluoromethyl)benzoyl]-1H-pyrazol-3-one (pyrasulfotole) together with N-(4-fluorophenyl)-6-[3-(trifluoromethyl)phenoxy]-2-pyridinecarboxamide (picolinafen), and its use as a herbicide in the control of broad-leaved weeds and grasses.

BACKGROUND OF THE INVENTION

[0002] Wild radish (Raphanus raphanistrum) is an abundant, widespread, broadleaf weed found throughout Australia. It is the cause of substantial losses in cereal crop yields. It is persistent, highly competitive and known for developing herbicide resistance. A herbicide is an active compound used to kill harmful plants. Wild radish is a significant problem for the cereal farmers in Western Australia, particularly for winter cereals.

[0003] A large number of herbicides are approved for use in Australia to control wild radish. The Australian Pesticides and Veterinary Medicines Authority (APVMA) have over 2,100 products approved for use in the control of wild radish. The actives include chlorsulfuron, imazamox, imazapyr, atrazine, diflufenican, 2,4-dichlorophenoxyacetic acid (2,4-D), dicamba, 2-methyl-4-chlorophenoxyacetic acid (MCPA), pyrasulfotole, bromoxynil, metasulam, flumetsulam, simazine and glyphosate.

[0004] Pyrasulfotole was discovered 20 years ago and it is effective against a wide range of broadleaf weeds found in fields of wheat, barley and triticale. Under the mode of action classifications, it is a group H / group 27 herbicide which inhibits the enzyme 4-hydroxyphenylpyruvate dioxygenase (HPPD) which impacts plant carotenoid pigment formation, and in turn leads to chlorophyll degradation. It was extremely successful commercially in Western Australia as wild radish was resistant to the other herbicides.

[0005] The group H / group 27 (HPPD) herbicides include isoxazoles such as isoxaflutole, pyrazoles such as benzofenap and pyrasulfotole, and trikeones such as bicyclopyrone and mesotrione, and also tembotrione.

[0006] Bayer launched the Precept® herbicide in Australia in 2008 and it was followed by the Velocity® herbicide. Both are emulsifiable concentrates which contain pyrasulfotole. Velocity® contains pyrasulfotole (37.5 g/L) and bromoxynil (210 g/L), the safener mefenpyr diethyl (9.4 g/L), solvent naphtha (petroleum) (381 g/L), propylene carbonate (114-228 g/L) fatty alcohol ethoxylate (34.2-114 g/L), calcium dodecylbenzene sulphonate (34.2-114 g/L), naphthalene (less than 57 g/L) and 2-ethylhexan-1-ol (less than 57 g/L).

[0007] Precept® contains pyrasulfotole (25 g/L), 2-methyl-4-chlorophenoxyacetic acid (MCPA) (125 g/L) and the safener mefenpyr diethyl (6.25 g/L), and solvent naphtha (petroleum) (262.5-315 g/L), benzyl alcohol (105-210 g/L), propylene carbonate (105-210 g/L), naphthalene (10.5-52.5 g/L) and 2-ethylhexan-1-ol (less than 21 g/L).

[0008] Pyrasulfotole is combined with bromoxynil or MCPA to improve herbicide efficacy. Bromoxynil is a group C / group 6 herbicide, these herbicides act by disrupting photosynthesis. MCPA is a group I / group 4 herbicide, a synthetic auxin. Both are effective against broadleaf plants.

[0009] Velocity® and Precept® herbicides have been commercially very successful and are sold worldwide. It is particularly useful in Western Australia for wild radish has developed resistance to many of the other herbicides.

[0010] Pyrasulfotole can damage cereal crops and is often combined with an appropriate crop safener, such as mefenpyr-diethyl which is used to safen cereal crops such as wheat and barley. Safeners operate by inducing the production of enzymes involved in herbicide detoxification in the protected plants but not the weed species.

[0011] N-(4-fluorophenyl)-6-[3-(trifluoromethyl)phenoxy]-2-pyridinecarboxamide, picolinafen is post-emergent herbicide used for broad-spectrum weed control in cereals. It was discovered before 1994 by Shell International Research and was acquired by American Cyanamid which, in turn, was acquired by BASF in 2000. BASF launched picolinafen in 2001 in Australia. It is also known as 4'-fluoro-6-(alpha,alpha,alpha-trifluoro-m-tolyloxy)pyridine-2-carboxanilide.

[0012] Picolinafen is a group F / group 12 herbicide, which are inhibitors of carotenoid biosynthesis. Other group F / group 12 herbicides include diflufenican, which is a pyridinecarboxamide, and norflurazon which is a pyridazinone.

[0013] Like many other herbicides, picolinafen has been used in the control of wild radish and broad-leaved weeds in cereals. One such product is Glocker® by Conquest Crop Protection which contains picolinafen 750 (g/kg) in a water dispersible granule.

[0014] Picolinafen can be combined with other actives. Paragon® by BASF contains picolinafen (50 g/L) with MCPA as 2-ethylhexyl ester (500 g/L), and sold as an emulsifiable concentrate. Flight EC by Nufarm contains Picolinafen (35g/L), bromoxynil as N-octanoyl ester (210 g/L) and MCPA as ethyl hexyl ester (350 g/L). Quadrant by Adama is a combination of picolinafen, diflufenican, bromoxynil and MCPA. These herbicides are used to control or suppress broadleaf weeds including wild radish in cereal crops.

[0015] Bayer has several patents directed to pyrasulfotole WO01/74785 (the compound), WO03/043422 (synergistic combinations of pyrasulfotole with bromoxynil or MCPA), WO03/043423 (pyrasulfotole with mefenpyr diethyl) and WO06/103002 (combination of pyrasulfotole with bromoxynil or MCPA, and a safener.

[0016] The Bayer patents suggest that their pyrasulfotole formulation could be combined with other specified active compounds in ready mixed formulations or in a tank mix. The lengthy list of additional actives suggested in WO01/74785 does not include picolinafen and very few combinations of pyrasulfotole with other actives appear to have been tested.

[0017] BASF has patents directed to herbicidal mixtures containing picolinafen. Australian patent AU 2004220342 discloses the combination of picolinafen, the safener mefenpyr and dicamba or quinmerac.

[0018] It is generally advantageous to provide alternative herbicide compositions to facilitate marketplace competition and because herbicide resistance can limit the ongoing utility of existing herbicides.

SUMMARY OF THE INVENTION

[0019] In an embodiment of the invention there is provided a herbicidal composition which includes pyrasulfotole together with picolinafen.

[0020] In a preferred embodiment the composition has a synergistically effective amount of pyrasulfotole and picolinafen.

[0021] In a preferred embodiment the weight ratio of pyrasulfotole to picolinafen is from 5:1 to 1:5, or from 4:1 to 1:2, or 2:1 to 1:2.

[0022] In a preferred embodiment the composition is applied to a field at a rate to provide from 5 to 50 g/ha of picolinafen, and/or from 5 to 100 g/ha of pyrasulfotole.

[0023] In an embodiment of the invention the herbicidal composition may include other herbicidally active compounds.

[0024] In a preferred embodiment the composition also includes a safener, preferably selected from mefenpyr-diethyl, oxabetrinil and cloquintocet, and any esters or salts thereof.

[0025] In a further embodiment of the invention there is provided a method of controlling or suppressing broad-leaved weeds including wild radish in a field by sequentially or simultaneously applying pyrasulfotole and picolinafen to that field.

[0026] In a further embodiment of the invention there is provided a method of controlling or suppressing broad-leaved weeds including wild radish in a field by applying the earlier described herbicidal composition to that field.

DETAILED DESCRIPTION OF THE INVENTION

[0027] The invention is a herbicidal composition of pyrasulfotole and picolinafen for use in the control or suppression of broad-leaved weeds and grasses including wild radish.

[0028] Pyrasulfotole and picolinafen have been previously supplied alone or with other actives for control or suppression of broad-leaved weeds, it is believed that they have not been used together for control or suppression of broad-leaved weeds.

[0029] Importantly, when two or more active compounds are used in combination, it is not uncommon for phenomena of physical and biological incompatibility to occur, for example insufficient stability of a joint formulation, decomposition of an active compound or antagonism of the active compounds.

[0030] The combination of pyrasulfotole and picolinafen unexpectedly provides synergistically enhanced activity, thus permitting the application rate to be reduced, compared with the individual application of the active compounds.

[0031] The compositions according to the invention are distinguished by the fact that the effective dosages of the herbicidal active compounds used in the combinations are reduced with respect to an individual dosage, so that it is possible to reduce the application rates due to the synergistic effect.

[0032] The activity of the combination of pyrasulfotole and picolinafen is more pronounced than the expected activity of individual pyrasulfotole and picolinafen. The synergistic effects permit the application rate to be reduced, a broader spectrum of broad-leaved weeds and weed grasses to be controlled, more rapid onset of the herbicidal action, a more prolonged action, better control of the harmful plants by only one application, or few applications, and widening of the period within which the product can be used. These properties are required in weed control practice to keep agricultural crops free from undesirable competing plants and thus to ensure and/or to increase quality and quantity of the yields.

[0033] The necessary application rate of the composition varies with the external conditions such as temperature, humidity, and the type of herbicide used. It can be varied within wide limits. Field application rates in the range from 0.001 to 10 kg, preferably from 0.001 to 2 kg, preferably from 0.005 to 0.100 kg, and more preferably from 0.005 to 0.05 kg for each of pyrasulfotole and picolinafen per hectare (kg/ha) is generally required.

[0034] The required field application rates and ratios of the herbicidal active compounds depend on numerous factors such as the target harmful plants, the field crops, the developmental stages of the plants, the climatic conditions, and the application technique.

[0035] The application rate of pyrasulfotole is generally from 0.01 to 2.0 kg/ha of the active substance. Preferably the application rate in g/ha is from 1 to 100, 5 to 80, 10 to 70, 12.5 to 60 and preferably 12.5 to 50 g/ha.

[0036] The application rate of picolinafen is generally from 0.01 to 0.5 kg/ha of the active substance. Preferably the application rate in g/ha is no more than 250, 125, 75, 50 or no more than 25 g/ha. The amount of picolinafen may be selected to avoid exceeding the maximum residue limit (MRL) in the relevant crop for the jurisdiction. The minimum amount can depend on weed resistance and may for example be selected from 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 g/ha. A preferred range can be from 5 to 50 and more preferably from 10 to 25 g/ha.

[0037] The ratios of the amount of the herbicidal active compounds pyrasulfotole and picolinafen can be varied within wide ranges. The molecular weight of pyrasulfotole and picolinafen are similar (362.33 and 376.3) and it can be easier to work with a weight ratio of pyrasulfotole to picolinafen.

[0038] The ratio of pyrasulfotole and picolinafen can be in the range selected from 1:50 to 50:1, from 1:20 to 20:1, from 1:10 to 10:1. Preferred weight ratios include from 5:1 to 1:5, from 5:1 to 1:4, from 4:1 to 1:3, and from 4:1 to 1:2. Ratios such as 2:1, 1:1, 1:2 are also preferred. The optimum ratio may depend on the field of application, on the weed spectrum and any other herbicidal active compounds used.

[0039] A preferred weight ratio is 4:1 to 1:2 pyrasulfotole and picolinafen. This is based on field application limits of 100 g/ha for pyrasulfotole and 25 g/ha of picolinafen. The combination of pyrasulfotole and picolinafen appears to be effective and synergistic at low ratios such a 1:2 ratio such as 12.5 g/ha of pyrasulfotole with 25 g/ha picolinafen.

[0040] A preferred formulation may be an emulsifiable concentrate containing 25 to 150 g/L of pyrasulfotole and an appropriate amount of picolinafen. The formulation could be diluted prior to use to provide an effective field application rate of pyrasulfotole from 12.5 to 100 g/ha and picolinafen from 10 to 25 g/ha.

[0041] A preferred formulation may be an emulsifiable concentrate containing 25, 37.5 or 50 g/L of pyrasulfotole and the same amount (25, 37.5 or 50 g/L) of picolinafen. In use, it could be diluted to provide application rates of pyrasulfotole of 25 g/ha and picolinafen of 25 g/ha.

[0042] Other formulation combinations include 50 g/L pyrasulfotole and 100, 50 or 25 g/L picolinafen for possible dilution to provide field application rates of 12.5 to 25, 25 to 25, 25 to 12.5 g/ha of pyrasulfotole to picolinafen.

[0043] The invention also provides a method for controlling unwanted vegetation, which includes applying the herbicide to the harmful plants, to parts of the harmful plants or to the area under cultivation.

[0044] The invention provides a method of controlling unwanted vegetation in a target crop or field, by applying a herbicidally effective amount of the herbicidal active compounds after mixing with water to the target crop or field.

[0045] Ideally, both the pyrasulfotole and picolinafen will be applied together in a joint application. However, the active compounds could be applied at different times in a sequential application. Joint or almost simultaneous application of the active compounds is preferred.

[0046] The compositions according to the invention can be employed for the selective control of annual and perennial monocotyledonous and dicotyledonous harmful plants in crops of cereals (for example barley, oats, rye, wheat), corn and rice and in crops of transgenic useful plants or crops of useful plants selected by classical means which are resistant to the herbicidal active compounds. Likewise, they can be employed for controlling undesirable harmful plants in plantation crops such as oil palm, coconut palm, Indian-rubber tree, citrus, pineapple, cotton, coffee, cocoa and the like, and also in fruit production and viticulture. Owing to their good compatibility, they are particularly suitable for use in cereals and corn, especially cereals.

[0047] The composition is preferably used for controlling unwanted harmful plants in corn and cereal crops such as, for example, wheat, rye, barley, oats, rice, sorghum, but also cotton, sugar beet, sugar cane and soybean, preferably cereals, rice and corn.

[0048] The crops being treated include but are not limited to common wheat (Triticum aestivum L.), barley (Hordeum vulgare L.), and triticale (Triticosecale spp.).

[0049] The composition can be used on crops which tolerate the action of herbicides owing to breeding, including genetic engineering methods. Suitable crops include genetically engineered cereals which are resistant against glyphosate or against herbicidal ALS Inhibitors, such as, for example, sulfonylureas or imidazolinones.

[0050] The compositions according to the invention act against a broad spectrum of weeds. They are suitable, for example, for controlling annual and perennial harmful plants such as, for example, from the species Abutilon, Alopecurus, Avena, Chenopodium, Cynoden, Cyperus, Digitaria, Echinochloa, Elymus, Galium, Ipomoea, Kochia, Lamium, Matricaria, Polygonum, Scirpus, Setaria, Sorghum, Veronica, Viola and Xanthium.

[0051] The compositions can be used in the effective control of broadleaf weeds present in Australian agriculture such as Raphanus raphanistrum, Brassica tournefortii, Polygonum aviculare, Amsinkia lycopsoides, Cicer arietinum, Vicia faba, Pisum sativum, Lens culinaris, Lupinus spp, Medicago sativa and Vicia sativa, to name a few.

[0052] The combination of pyrasulfotole and picolinafen may offer other advantages over existing pyrasulfotole formulations. It is expected that a satisfactory herbicidal control or suppression of wild radish can be obtained for the same or less cost than the market leading Velocity® herbicide.

[0053] The herbicidal compositions according to the invention can be prepared and provided as a mixed formulation of pyrasulfotole and picolinafen, optionally together with other customary formulation auxiliaries, which mixed formulations are then applied to the field in the usual manner as after dilution with water, or else they can be prepared in the form of so-called tank mixes by joint dilution with water of the components which are formulated separately, or partly separately.

[0054] There can be significant variability in weed type, weed resistance and weed infestation from paddock to paddock, and farm enterprises need the option vary the applied herbicides and the amounts. Tank mixing herbicides is important to modern farming practices and is considered by some to be key to herbicide resistance management. The addition of an additional herbicide in a tank-mix can provide improved weed control and may allow farmers to use smaller amounts of herbicides for a longer period before they become ineffective.

[0055] In an embodiment, the invention provides tank mixing pyrasulfotole with picolinafen and applying the mixed formulation to the field. Additional formulation auxiliaries could be tank mixed or may be present with either or both pyrasulfotole or picolinafen in a readymix formulation.

[0056] The herbicidal composition may include other agrochemical compounds such as other herbicides or adjuvants. It may also include other components such as fertilizers, for example ammonium nitrate, urea, mineral salt solutions employed for treating nutritional and trace element deficiencies.

[0057] The composition may be used with or include a safener, more specifically an antidote-effective amount of the safener, being an amount of one or more safeners suitable for at least partially counteracting the phytotoxic effect of a herbicide or herbicide mixture on a useful plant. The present invention includes combinations of pyrasulfotole and picolinafen with a safener.

[0058] A safener is understood as meaning a compound which compensates for, or reduces, the phytotoxic properties of a herbicide with regard to useful plants, without substantially reducing the herbicidal activity against harmful plants. A safener does not normally contribute to herbicidal activity. Finding a safener for a specific group of herbicides can be a difficult task since the mechanisms by which a safener reduces the harmful action of herbicides are not known in detail.

[0059] A safener reduce or compensate for phytotoxic effects which may occur when using the herbicidally active compounds in crops of useful plants without essentially adversely

affecting the efficacy of these herbicidally active compounds against harmful plants. Thus, the field of application of conventional crop protection agents can be widened considerably and extended to, for example, crops such as wheat, barley, rice and corn in which the use of the herbicides has previously not been possible or only with limitations, that is to say at low dosages with a narrow spectrum of action. The herbicidally active compounds and the safeners mentioned can be applied together as ready-mix formulations or by the tank mix method or sequentially in any desired sequence.

[0060] The weight ratio of safener to herbicidally active compound may vary within wide limits and is preferably in the range of from 1:100 to 100:1, in particular from 1:10 to 10:1. The optimum amounts of herbicidally active compound and safener depend in each case on the type of the herbicidally active compound used or on the safener used and on the nature of the plant stock to be treated and can be determined in each individual case by simple routine preliminary experiments.

[0061] The seed of the crop plant may be pre-treated with the safener or introduced into the seed furrows prior to sowing or used together with the herbicide before or after emergence of the plants. Pre-emergence treatment includes not only the treatment of the area under cultivation before sowing, but also the treatment of the sown soil which does not yet sustain vegetation.

[0062] Preferably, the safener will be applied together with the herbicide composition. A tank mix or readymix may be employed for this purpose. The safener application rates required may vary within wide limits, depending on the indication and the herbicidally active compound used; but in general, they are in the range of from 0.001 to 5 kg, preferably from 0.01 to 0.5 kg, of safener per hectare.

[0063] Preference is given to safeners selected from one or more of mefenpyr-diethyl, oxabetrinil, cloquintocet or cloquintocet mexyl, fenclorim, isoxadifen, fluxofenim, flurazole, dichiormid, benoxacor, furilazole, 4-dichloroacetyl-1 -oxa-4-aza-spiro[4,5]decane.

[0064] More preferably the safener is selected from one or more of mefenpyr-diethyl, oxabetrinil, or cloquintocet mexyl. The mefenpyr-diethyl, cloquintocet mexyl and oxabetrinil

are approved for use in Australia and mefenpyr-diethyl is used with pyrasulfotole in Velocity® and Precept® for cereal crops, and cloquintocet mexyl has been used to safen wheat.

[0065] Cloquintocet is (5-Chloroquinolin-8-yloxy)acetic acid. It can be used in the acid form or more commonly as the 1-methylhexyl ester known as Cloquintocet-mexyl.

[0066] Mefenpyr-diethyl is diethyl 1-(2,4-dichlorophenyl)-5-methyl-4H-pyrazole-3,5-dicarboxylate. It may be preferred safener from a customer perspective as pyrasulfotole and mefenpyr-diethyl have been used together for many years in the Velocity®and Precept® herbicides. Likewise, it is preferably to use 4:1 ratio on a g/L basis of pyrasulfotole to mefenpyr-diethyl.

[0067] The herbicidal composition can be used in the form of directly sprayable aqueous solutions, powders, suspensions, concentrated aqueous, oily or other suspensions or dispersions, emulsions, oil dispersions, pastes, dusts and granules, by means of spraying, atomizing, dusting, spreading or watering. The form to be used can depend on the intended purposes; but should ensure an even distribution of the active composition.

[0068] The composition may be formulated in various ways, depending on the prevailing biological and/or chemico-physical parameters. Suitable possibilities of formulation are, for example, wettable powders (WP), emulsifiable concentrates (EC), aqueous solutions (SL), water-soluble powders, water-soluble concentrates, emulsions (EW) such as oil-in-water and water-in-oil emulsions, sprayable solutions or emulsions, capsule suspensions, oil- or water-based dispersions, suspoemulsions, suspension concentrates, dusts (DP), oil-miscible solutions seed-dressing products, granules (GR) in the form of microgranules, spray granules, coated granules and absorption granules, granules for soil application or broadcasting, water-soluble granules, water-dispersible granules (WDG), ULV formulations, microcapsules and waxes.

[0069] These formulation types are well known and are described, for example, in: Winnacker-Kuchler, "Chemische Technologie" [Chemical engineering], Volume 7, C. Hauser Verlag Munich, 4th Ed., 1986; Wade van Valkenburg, "Pesticide Formulations", Marcel Dekker 1973; K. Martens, "Spray Drying Handbook", 3rd Ed. 1979, G. Goodwin Ltd. London. The

formulation auxiliaries which may be required, such as inert materials, surfactants, solvents and further additives are likewise known and described, for example, in: Watkins, "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Darland Books, Caldwell H.v. Olphen, "Introduction to Clay Colloid Chemistry"; 2nd Ed., J. Wiley Sons, C. Marsden, "Solvents Guide"; 2nd Ed., Interscience, N.Y. 1963; McCutcheon's "Detergents and Emulsifiers Annual", MC Publ. Corp., Ridgewood Sisley and Wood, "Encyclopedia of Surface Active Agents", Chem. Publ. Co. Inc., N.Y. 1964; Schonfeldt, "Grenzflachenaktive Athylenoxidaddukte" [Surface-active ethylene oxide adducts], Wiss. Verlagsgesell., Stuttgart 1976; Winnacker-Kuchler, "Chemische Technologie", Volume 7, C. Hauser Verlag Munich, 4th Ed. 1986.

[0070] Based on these formulations, combinations with other crop protectants such as insecticides, acaricides, herbicides, fungicides, and with safeners, fertilizers and/or growth regulators may also be prepared, for example in the form of a readymix or a tank mix.

[0071] Wettable powders are preparations which are uniformly dispersible in water and which, besides the active compound, additionally comprise ionic and/or nonionic surfactants (wetters, dispersants), for example polyoxethylated alkylphenols, polyoxethylated fatty alcohols, polyoxethylated fatty amines, fatty alcohol polyglycol ether sulfates, alkanesulfonates, alkylbenzenesulfonates, sodium lignosulfonate, sodium 2,2'-dinaphthylmethane-6,6'-disulfonate, sodium dibutylnaphthalenesulfonate, or else sodium oleoylmethyltaurinate, in addition to a diluent or inert substance.

[0072] To prepare the wettable powders, the herbicidally active compounds are ground finely, for example in customary apparatuses such as hammer mills, blower mills and air-jet mills, and simultaneously or subsequently mixed with the formulation auxiliaries.

[0073] In wettable powders, the herbicidal active compounds are, for example, from approximately 10 to 90% by weight, the remainder to 100% by weight being composed of customary formulation components. The powder may contain 25% of the active compound mixture and approximately 65% kaolin containing quartz as an inert substance and 10% potassium lignosulfonate together with 1% sodium oleoylmethyltaurinate as wetting agent and dispersant.

[0074] Emulsifiable concentrates (EC) are normally a homogeneous, liquid formulation for application as an emulsion after dilution in water. The emulsifiable concentrate will contain a pesticide in an organic solvent system together with emulsifier(s).

[0075] Emulsifiable concentrates are a common form of agricultural and farming chemicals as they can have a low production cost and involve simple technology. Emulsifiable concentrates may be tank mixed or otherwise combined with water and possibly other additives to form a field formulation. The field formulation can then be applied to paddocks or crops by boom spraying and the like, to deliver the pesticide to the fields or crop.

[0076] An emulsifiable concentrate normally contains one or more pesticides, solvents, emulsifiers as well as additives such as stabilizers, antifoaming agents and the like.

[0077] Emulsifiable concentrates are prepared for example by dissolving the herbicidal active compounds in an organic solvent, for example butanol, cyclohexanone, DMF or else high-boiling hydrocarbons such as saturated or unsaturated aliphatic or alicyclic substances, aromatic substances or mixtures of these organic solvents with addition of one or more ionic and/or nonionic surfactants (emulsifiers). The concentration of herbicidal active compounds amounts to approximately 1 to 80% by weight of herbicidal active compounds.

[0078] Solvents suitable for use with the herbicidal active compounds include petroleum fractions solvent derives from crude oil via either gas condensation or petroleum distillation. These include, aliphatic paraffins, olefins, naphthene constituents, aromatics and the like, in different proportions. A preferred petroleum fractions solvent is a petroleum naphtha, more preferably a heavy aromatic naphtha solvent such as Solvesso 100, Solvesso 100S, Solvesso 150, Solvesso 150ND, Solvesso 200 or Solvesso 200ND. Solvesso is a product from ExxonMobil Chemical.

[0079] The amount of solvent depends on the desired concentration as well as physical limits. Emulsifiable concentrates having higher concentrations of the herbicidal active compounds are preferred but it can be difficult to prepare a stable concentrate.

[0080] In an embodiment there is provided an emulsifiable concentrate which contains pyrasulfotole in petroleum fractions solvent, the solvent being at least 450 g/L, more

preferably at least 475 g/L, more preferably at least 500 g/L, more preferably at least 525 g/L, most preferably at least 550 g/L of the emulsifable concentrate.

[0081] The concentrate may require an additional solvent when preparing higher concentrations of the herbicidal active compounds. The additional solvent may be selected from pyrrolidones including N-alkylated pyrrolidones such as n-methyl pyrrolidone and glycol ethers such as diethylene glycol monomethyl ether (Carbitol), ethylene glycol monobutyl ethers (Butyl Glysolv), propylene glycol monomethyl ether (Glysolv PM) and the like. Preferably the additional solvent is N-methyl pyrrolidine.

[0082] The anionic and the non-ionic emulsifier may each comprise one or more emulsifiers. Often a mixture of emulsifiers is required to provide the desired properties. Possible emulsifiers include calcium alkylarylsulfonates such as calcium dodecylbenzenesulfonate, or nonionic emulsifiers such as fatty acid polyglycol esters, alkylaryl polyglycol ethers, fatty alcohol polyglycol ethers, propylene oxide/ethylene oxide condensates, alkyl polyethers, sorbitan esters such as, for example, sorbitan fatty acid esters or polyoxyethylene sorbitan esters such as polyoxyethylene sorbitan fatty acid esters.

[0083] The anionic emulsifier may be selected from carboxylates, sulphonates, sulphated alkanolamides, petroleumsulphonates, alkylbenzenesulphonates, olefin sulphonates, naphthalenesulphonates, sulphates, alkylsulphates, sulphates and sulphonates of oils and fatty acids, sulphated esters, ethoxylated and/or sulphonated alkylphenols. The anionic emulsifier is preferably calcium alkyl benzene sulphonate (CABS).

[0084] CABS is highly viscous and for ease of handling it is normally provided dissolved in a solvent. The solvent should be a high flash point, aromatic-free solvent such as 2-ethyl hexanol, solvent naphtha and/or 1-hexanol. Suitable commercial formulations of CABS include Nansa EVM 70/2E and Trisol 460, both of which have CABS dissolved in 2-ethyl hexanol, solvent naphtha and/or 1-hexanol at approximate ratio of 60% CABS to 40% solvent. CABS may be present in the concentrate an amount of 10 to 20 g/l.

[0085] A broad range of nonionic emulsifiers may be used and include alkoxylated alcohols, alkoxylated block polymers, alkoxylated alkylphenols, alkoxylated monostyryl phenols,

alkoxylated distyryl phenols, alkoxylated tristyryl phenols, alkoxylated amines, alkoxylated amides, alkoxylated fatty esters, alkoxylated fatty acids, and the like.

[0086] The nonionic emulsifier is suitably selected from the group consisting of alkoxylated alkylphenol (e.g., Termul 200), alkoxylated vegetable oil (e.g. Termul 1285 or Termul 1284), Ethoxylated tallow amine (e.g., Terwet 3784), alkoxylated tristyryl phenol (e.g., Termul 3150) or an alkyl polyoxyalkylene ether (e.g., Termul 203). The preferred nonionic emulsifiers include Castor Oil Polyglycol Ethers, such as the Termul 1284 and Termul 1285 products, and Alkyl polyoxyalkylene ethers such as the Termul 203 product.

[0087] Dusts are obtained in general by grinding the herbicidal active compounds with finely divided solid materials, for example talc, natural clays such as kaolin, bentonite and pyrophyllite, or diatomaceous earth. Typically, the herbicidal active compounds comprise from approximately 1 to 20% by weight of the dust.

[0088] Suspension concentrates may be water- or oil-based. They can be prepared for example by wet milling by means of commercially available bead mills, if appropriate with addition of surfactants as, for example, have already been listed above in the case of the other formulation types.

[0089] Emulsions, for example oil-in-water emulsions can be prepared for example by means of stirrers, colloid mills and/or static mixers using aqueous organic solvents and, if appropriate, surfactants as, for example, have already been listed above in the case of the other formulation types.

[0090] Granules can be produced either by spraying the herbicidal active compounds onto adsorptive granulated inert material or by applying active compound concentrates to the surface of carriers such as sand, kaolinite or of granulated inert material by means of binders, for example polyvinyl alcohol, sodium polyacrylate or else mineral oils. The content of herbicidal active compounds in the water-dispersible granules is between 10 and 90% by weight

[0091] Suitable active compounds may also be granulated in the manner which is conventional for the production of fertilizer granules, if desired as a mixture with fertilizers. Water-dispersible granules are prepared by the customary methods such as spray-drying, fluidized-bed granulation, disk granulation, mixing by means of highspeed mixers, and extrusion without solid inert material. To prepare disk, fluidized-bed, extruder and spray granules, see, for example, methods in "Spray-Drying Handbook" 3rd ed. 1979, G. Goodwin Ltd., London; J.E. Browning, "Agglomeration", Chemical and Engineering 1967, pages 147 et seq.; "Perry's Chemical Engineer's Handbook", 5th Ed., McGraw-Hill, New York 1973, pp. 8-57. For further details on the formulation of crop protection agents see, for example, G.C. Klingman, 'Weed Control as a Science", John Wiley and Sons, Inc., New York, 1961, pages 81-96 and J.D. Freyer, S.A. Evans, 'Weed Control Handbook", 5th Ed., Blackwell Scientific Publications, Oxford, 1968, pages 101-103.

[0092] In addition, the composition formulations include, if appropriate, the adhesives, tackifiers, wetting agents, surfactants, dispersants, emulsifiers, penetrants, preservatives, antifreeze agents, solvents, fillers, carriers, colorants, antifoams, evaporation inhibitors, pH regulators, and viscosity regulators.

[0093] Inert additives include medium to high boiling point mineral oil fractions, such as kerosene and diesel oil, coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example paraffin, tetrahydro naphthalene, alkylated naphthalenes or derivatives thereof, alkylated benzenes or derivatives thereof, alcohols, such as methanol, ethanol, propanol, butanol, cyclohexanol, ketones, such as cyclohexanone, strongly polar solvents, such as N-methyl- pyrrolidone or water.

[0094] Possible surfactants include the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, for example ligno-, phenol-, naphthalene- and dibutylnaphthalenesulfonic acid, and of fatty acids, alkyl- and alkylarylsulfonates, alkyl sulfates, lauryl ether sulfates and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, and also of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenyl or tributylphenyl polyglycol

ether, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors or methylcellulose.

[0095] For use, the formulations, which are in commercially available form, are, if appropriate, diluted in a customary manner, for example using water in the case of wettable powders, emulsifiable concentrates, dispersions and water-dispersible granules. These are readymix formulations.

[0096] Preparations in the form of dusts, soil granules, granules for spreading and sprayable solutions are conventionally not diluted any further with other inert substances prior to use.

[0097] A possible use is the joint application of the active compounds in the form of tank mixes, where the concentrated formulations of the individual active compounds, in the form of their optimal formulations, are mixed jointly with water in the tank, and the spray mixture obtained is applied. A joint herbicidal formulation of the herbicidal compositions according to the invention has the advantage that it can be applied more easily because the amounts of the components have already been adjusted with respect to one another to the correct ratio. Moreover, the auxiliaries of the formulation can be selected to suit each other in the best possible way, while a tank mix of various formulations may result in undesirable combinations of auxiliaries.

[0098] The herbicidal compositions can be applied by the pre-emergence or by the post-emergence method. If the active compounds are less well tolerated by certain crop plants, application techniques may be used in which the herbicidal compositions are sprayed, with the aid of the spraying equipment, in such a way that they come into as little contact as possible, if any, with the leaves of the sensitive crop plants, while the active compounds reach the leaves of the undesirable plants growing underneath, or the bare soil surface.

[0099] In the case of post-emergence treatment, the herbicidal compositions according to the inventions are applied to the plants mainly by spraying the leaves. Here, the application can be carried out by customary spraying techniques using, for example, with water as the carrier.

[0100] In an embodiment a spray mixture formed from a tank mix or a readymix formulation having the composition is applied at a rate of about 5 to about 1,000 g per hectare (e.g., about 5g, 10g, 15g, 20g, 25g, 30g, 35g, 40g, 45g, 50g, 55g, 60g, 65g, 70g, 75g, 80g, 85g, 90g, 95g, 100g, 105g, 110g, 115g, 120g, 125g, 130g, 135g, 140g, 145g, 150g, 155g, 160g, 165g, 170g, 175g, 180g, 185g, 190g, 195g, 200g, 205g, 210g, 215g, 220g, 225g, 230g, 235g, 240g, 245g, 250g, 255g, 260g, 265g, 270g, 275g, 280g, 285g, 290g, 295g, 300g, 305g, 310g, 315g, 320g, 325g, 330g, 335g, 340g, 345g, 350g, 355g, 360g, 365g, 370g, 375g, 380g, 385g, 390g, 395g, 400g, 405g, 410g, 415g, 420g, 425g, 430g, 435g, 440g, 445g, 450g, 455g, 460g, 465g, 470g, 475g, 480g, 485g, 490g, 495g, 500g, 505g, 510g, 515g, 520g, 525g, 530g, 535g, 540g, 545g, 550g, 555g, 560g, 565g, 570g, 575g, 580g, 585g, 590g, 595g, 600g, 605g, 605g, 610g, 615g, 620g, 625g, 630g, 635g, 640g, 645g, 650g, 655g, 660g, 665g, 670g, 675g, 680g, 685g, 690g, 695g, 700g, 705g, 710g, 715g, 720g, 725g, 730g, 735g, 740g, 745g, 750g, 755g, 760g, 765g, 770g, 775g, 780g, 785g, 790g, 795g, 800g, 805g, 810g, 815g, 820g, 825g, 830g, 835g, 840g, 845g, 850g, 855g, 860g, 865g, 870g, 875g, 880g, 885g, 890g, 895g, 900g, 905g, 910g, 915g, 920g, 925g, 930g, 935g, 940g, 945g, 950g, 955g, 960g, 965g, 970g, 975g, 980g, 985g, 990g, 995g, 1,000g per hectare and any range therein.

[0101] The compounds of the composition may be present and used both in the form of the pure enantiomers and as racemates or diastereomer mixtures, if they exist.

[0102] The compounds may be present and used in the form of their agriculturally useful salts and, if the compounds are carboxylic acids, also in the form of their agriculturally useful esters, thioesters and amides, such they exist.

[0103] The herbicidal compositions may contain other herbicidally active compounds such as other compounds for the control of wild radish. The other actives may include one or more selected from chlorsulfuron, imazamox, imazapyr, atrazine, diflufenican, 2,4-dichlorophenoxyacetic acid (2,4-D), dicamba, 2-methyl-4-chlorophenoxyacetic acid, bromoxynil, metasulam, flumetsulam, simazine, glyphosate, isoproturon, metribuzin, propanil, glufosinate, clomazone, acetochlor, alachlor, anilofos, flufenacet, metolachlor, thenylchlor flufenacet, mefenacet, mecoprop, dicamba, diflufenzopyr fluroxypyr and quinclorac. Combinations with bromoxynil, MCPA and diflufenican may be preferred as these

actives have a longer lasting herbicidal effect, which can provide benefits with ongoing weed management.

EXPERIMENTAL – Wild Radish Glasshouse trials

[0104] Twenty seeds of wild radish (Raphanus raphanistrum) were sown in each 100mm x 100mm sample pot containing a potting mix (50% peatmoss, 25% pine bark, 25% river sand with approximately 6% organic carbon). The wild radish was grown to provide plants at the four-leaf stage.

[0105] The wild radish seeds used in the sample pots were sourced from three different Australian farm sites to provide three distinct biotypes. The three biotypes are referred to as populations A, B and C. Sufficient seeds and pots were used to provide three trials for each population type and for each formulation.

[0106] Glocker® 750 from Conquest Crop Protection Pty Ltd was used for the picolinafen and it contains 750 g/kg of picolinafen as water-dispersible granules. A picolinafen solution was prepared by combining and vigorously agitating Glocker® granules with water. The concentration was selected to provide an effective dosage rate of 25 g/ha of picolinafen, being a picolinafen dosage rate already in use for cereals in Australia.

[0107] Magnitude® from Conquest Crop Protection Pty Ltd was used for the pyrasulfotole. It is an emulsifiable concentrate containing a 4:1 g/L ratio of pyrasulfotole and mefenpyr diethyl safener. It was added to the picolinafen solution and mixed to provide test herbicide solutions. The emulsifiable concentrate contained containing 100 g/L of pyrasulfotole (102 g of pyrasulfotole technical grade, purity 98%) and 25 g/L of mefenpyr-diethyl (26.3 g of mefenpyr diethyl technical grade purity 95%) in a petroleum distillate (solvesso 150) and emulsifiers.

[0108] The amount of pyrasulfotole added to the test herbicide solutions was selected to provide an effective dosage rate of 12.5, 25, 37.5 and 50 g/ha of pyrasulfotole.

[0109] Control solutions containing effective dosage rates of 12.5, 25, 37.5 and 50 g/ha pyrasulfotole with mefenpyr diethyl safener, and 25 g/ha of picolinafen were prepared for use in the Colby calculations.

[0110] A Velocity® herbicide solution having 37.5g/L of pyrasulfotole and 210g/l of bromoxynil was tested for comparative purposes. The solution was applied at an effective dosage rate of 25.1g/ha of pyrasulfotole and 141 g/ha of bromoxynil.

[0111] Glisarin 704 from Conquest was added to the test and control solutions at an effective rate of 1% v/v of the solution. Glisarin is a spray adjuvant containing ethyl and methyl esters of free fatty acids from canola oil and it is commonly used to enhance the physical properties of the spray mixture. It is useful in keeping the spray droplets within the preferred size and helps to retain the herbicide on the plant leaf.

[0112] The test and control herbicide solutions were prepared at least 30 minutes before application to allow the active compounds to be fully dispersed in water. Bottles containing the solutions were vigorously agitated at least 10 times before the solution was applied to the sample pots.

[0113] The test and control solutions were delivered in a single pass by using a twin-nozzle laboratory sprayer calibrated to deliver 110 L of water per ha at 210 kPa and mounted with flat spray tips (Teejet XR) producing fine droplets.

[0114] Plant survival was measured by survivors actively growing after herbicide treatments. Survivors were defined as plants that grew after herbicide treatments. Plant growth based on visual estimation of the aboveground biomass of the survivors relative to untreated controls was assessed 28 days after herbicide treatments

[0115] Each herbicide solution was applied to three replicated pots and the results combined in the tables below. Each table relates to a distinct biotype population A, B or C of Raphanus raphanistrum, having different resistance to the Velocity® herbicide.

[0116] The observed control percentage was calculated by determining plant survival as percentages less plants survived / number of seedlings treated with herbicides.

[0117] The Colby value was determined using the Colby equation to assess the type of interaction between the tested herbicides. E= (A + B)-[(A x B)/100] E is the expected level of weed control as a percentage for an additive interaction of herbicides A & B, A is the percentage of observed control with pyrasulfotole, and B is the percentage of weed control with picolinafen. There is a synergistic interaction between the active herbicides when the observed control percentage of the herbicide components exceeds the Colby value – the calculated additive effect of same herbicide components.

[0118] The herbicidal efficacy was assessed on Populations A, B and C showed varying resistance to Velocity®, Picolinafen and Pyrasulfotole.

[0119] Table 1: Population A

Herbicide (Amount g/ha)	Observed Control	Colby Value
Velocity® Pyrasulfotole (25) & Bromoxynil (140)	67%	-
Velocity® Pyrasulfotole (37.5) & Bromoxynil (210)	70%	-
Picolinafen (25)	7%	-
Pyrasulfotole (12.5)	0%	-
Pyrasulfotole (25)	15%	-
Pyrasulfotole (37.5)	24%	-
Pyrasulfotole (50)	30%	-
Picolinafen (25) & Pyrasulfotole (12.5)	63%	7%
Picolinafen (25) & Pyrasulfotole (25)	92%	21%
Picolinafen (25) & Pyrasulfotole (37.5)	73%	29%
Picolinafen (25) & Pyrasulfotole (50)	90%	35%

[0120] Population A was highly resistant to picolinafen alone (control < 50%) and moderately resistant to Velocity® (control < 80%). The combination of pyrasulfotole and picolinafen provided a surprisingly effective herbicide composition and effective control of this wild radish population.

[0121] Table 2: Population B

Herbicide (Amount g/ha)	Observed Control	Colby Value
Velocity® Pyrasulfotole (25) & Bromoxynil (140)	56%	-
Velocity® Pyrasulfotole (37.5) & Bromoxynil (210)	62%	-
Picolinafen (25)	48%	-
Pyrasulfotole (12.5)	19%	-
Pyrasulfotole (25)	21%	-
Pyrasulfotole (37.5)	36%	-
Pyrasulfotole (50)	31%	-
Picolinafen (25) and Pyrasulfotole (12.5)	88%	58%
Picolinafen (25) and Pyrasulfotole (25)	81%	59%
Picolinafen (25) and Pyrasulfotole (37.5)	93%	67%
Picolinafen (25) and Pyrasulfotole (50)	93%	64%

[0122] Population B of Australian wild radish had the highest resistance to Velocity® out of the 3 populations and the combination of pyrasulfotole with picolinafen provided an effective means for controlling those resistant weeds.

[0123] Table 3 – Population C

Herbicide (Amount g/ha)	Observed Control	Colby Value
Velocity® Pyrasulfotole (25) & Bromoxynil (140)	69%	-
Velocity® Pyrasulfotole (37.5) & Bromoxynil (210)	100%	
Picolinafen (25)	70%	-
Pyrasulfotole (12.5)	45%	-
Pyrasulfotole (25)	44%	-
Pyrasulfotole (37.5)	55%	-
Pyrasulfotole (50)	45%	-
Picolinafen (25) and Pyrasulfotole (12.5)	96%	84%
Picolinafen (25) and Pyrasulfotole (25)	100%	83%
Picolinafen (25) and Pyrasulfotole (37.5)	100%	86%
Picolinafen (25) and Pyrasulfotole (50)	100%	84%

[0124] Population C was the most susceptible to Pyrasulfotole of the three tested populations. The trial results showed that the combination of pyrasulfotole and picolinafen provided the same or more effective control than Velocity® against a susceptible population. The trial results suggest an effective control of wild radish in Australia can be provided at a reduced herbicide cost relative to Velocity®.

[0125] The statistical analysis of pooled values across the three wild radish populations as mean values of observed control (%) vs. Colby expected control (%) indicated pyrasulfotole synergized with picolinafen. The observed control of wild radish with pyrasulfotole and picolinafen ranged well above the expected additive herbicide interaction as calculated by the Colby equation.

EXPERIMENTAL – Field Trial with Wheat (Triticum aestivum)

[0126] A randomized complete block (RCB) trial was undertaken in 2022, in Bolgart, Western Australia. It was conducted with farmer sown Chief CL wheat (Triticum aestivum) in a sandy loam soil. The site had a seeding rate was 60 kg/ha at a depth of 3 centimetres and was sown at a speed of 8.5 kilometres per hour. The field was divided into plots with each plot being was 2.5 metres in width and 12 metres in length. The trial contained three replications of

plots for each treatment and the results were combined in the table below. The trial compared the effectiveness of a formulation containing Pyrasulfotole and Picolinafen with Velocity® on wild radish (Raphanus raphanistrum).

[0127] The field trials involved Velocity® from Bayer, an emulsifiable concentrate containing Pyrasulfotole (37.5 g/L) and Bromoxynil, present as Octanoate (210 g/L) and the safener Mefenpyr diethyl (9.4 g/L); Magnitude® from Conquest Crop Protection, an emulsifiable concentrate containing Pyrasulfotole (100 g/L) and Mefenpyr diethyl (25 g/L); Glocker® from Conquest Crop Protection, a water dispersible granule formulation containing Picolinafen (750 g/kg); and In2 Pro, from Conquest Crop Protection, an emulsifiable concentrate containing nonyl phenol ethoxylate surfactant (240 g/L) and Paraffinic oil (582 g/L).

[0128] The plots were treated when the wheat was at the growth stage of GS15 (fifth leaf development) to GS21 (tillering – main shoot and one tiller) and the weed size was between 3-5 leaf. The herbicide solutions were prepared by mixing the appropriate amount of the products with 2000 mL of water and vigorously agitated. The herbicide solutions were prepared at least 30 minutes before the solution was applied to plots. The herbicide solutions were applied using a 2-meter handheld boom sprayer with four flat air induction nozzles by Agrotop at a spacing of 50 cm designed to deliver 100 L of water volume per hectare at 250 kPa from a height 50 cm from the ground. At application, all herbicide solutions contained the adjuvant In2 Pro at 0.5 % v/v. At the time of application there was a partial cloud cover, with a temperature of 12°C and a relative humidity of 85%. The wind speed at time of application was 13 km/hr.

[0129] Radish control was measured 14, 24 and 43 days after application (DAA). In the first two assessment days (12 DAA and 24 DAA) a visual, universal weed rating on a scale of 0-100% based on weed reduction in size and/or numbers in relation to untreated control plots was conducted. On the last assessment (43 DAA) the number of surviving wild radish plants were counted in each plot and compared with the number of survivors found in the untreated to give a percentage control.

[0130] Table 4 – Comparative Field Trials – Wheat

Herbicide (g/ha)	Radish Control %		
	14 DAA	24 DAA	43 DAA
Untreated control	0	0	0
Velocity® PST (12.5) Brom (70)	82	92	98
Velocity® PST (25) Brom (140)	93	93	96
Velocity® PST (37.5) Brom (210)	98	97	100
Velocity® PST (50) Brom (280)	100	100	100
Magnitude® & Glocker® PST (12.5) PICO (25)	93	100	98
Magnitude® & Glocker® PST (25) PICO (25)	100	100	99
Magnitude® & Glocker® PST (37.5) PICO (25)	100	100	100
Magnitude® & Glocker® PST (50) PICO (25)	100	100	100

In the tables PST is Pyrasulfotole, Brom is Bromoxynil and PICO is Picolinafen.

[0131] The results show surprisingly excellent wild radish control when the combination of pyrasulfotole and picolinafen is applied in a more practical setting. The results showed that there were no statistically significant differences between the invention and the industry standard when the pyrasulfotole grams active per hectare were the same.

EXPERIMENTAL – FIELD TRIAL Wheat

[0132] A RCB trial was undertaken in 2022, Geraldton Western Australia, in farmer sown Spartacus CL barley (Hordeum vulgare) in a sandy loam soil. The site had a seeding rate was 60 kg/ha at a depth of 3 centimetres and was sown at a speed of 8.5 kilometres per hour. The field was divided into plots with each plot being was 2.5 metres in width and 12 metres in length. The trial contained three replications of plots for each treatment and the results were combined in the table below.

[0133] The herbicide solutions were applied to the plots using a 2-meter handheld boom sprayer with four flat air induction nozzles by Agrotop at a spacing of 50 cm designed to deliver 100 L of water volume per hectare at 250 kPa from a height 50 cm from the ground. The plots were treated when the barley was at a growth stage of GS15- GS21 and weed size

of between 3-5 leaf. Herbicide solutions were prepared by mixing the products with 2000 mL of water and vigorously agitated. The herbicide solutions were prepared at least 30 minutes before the solution was applied to plots.

[0134] Plant survival was measured 12 and 24 days after application (DAA) via Radish Control: A visual, universal weed rating on a scale of 0-100% based on weed reduction in size and/or numbers in relation to untreated control plots.

[0135] Table 5 – Comparative Field Trials – Barley

Herbicide (g/ha)	Radish Control %	
	14 DAA	24 DAA
Untreated control	0	0
Velocity® PST (25) Brom (140)	97	96
Velocity® PST (37.5) Brom (210)	100	100
Magnitude® and Glocker® PST (25) PICO (25)	100	99
Magnitude® and Glocker® PST (25) PICO (37.5)	100	100

[0136] The results show excellent wild radish control when the combination of pyrasulfotole and picolinafen is applied in field conditions. The results suggest the combination of common farmer practices with the invention would provide excellent in-crop results for the control of wild radish.

[0137] Additional field trials were conducted on wild radish in wheat and barley fields by applying pyrasulfotole (25 g/ha) and picolinafen (25 g/ha) in combination with varying amounts of additional herbicides selected from bromoxynil, MCPA and diflufenican, (alone and in combination). Due to the effectiveness of pyrasulfotole and picolinafen at the applied rate, it is unclear whether bromoxynil, MCPA and diflufenican had any immediate impact on radish control. As the formulation remained fully effective, it is expected that there was no antagonistic interaction between any and all of bromoxynil, MCPA and diflufenican and the synergistic combination of pyrasulfotole and picolinafen. Bromoxynil, MCPA and diflufenican have a longer lasting herbicidal residual effect than pyrasulfotole and picolinafen, measured in weeks rather than days, such that it can be beneficial to combine one or more of least

bromoxynil, MCPA and diflufenican, or similar herbicides with pyrasulfotole and picolinafen, for longer lasting weed control.

[0138] Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

[0139] The reference to any prior art in this specification is not and should not be taken as an acknowledgement or any form of suggestion that the prior art forms part of the common general knowledge.

CLAIMS

1. A herbicidal composition which includes pyrasulfotole together with picolinafen.
2. The composition of claim 1 having a synergistic effective amount of pyrasulfotole and picolinafen.
3. The composition of claim 1 containing from 5:1 to 1:5 weight ratio of pyrasulfotole to picolinafen.
4. The composition of claim 1 containing from 4:1 to 1:2 weight ratio of pyrasulfotole to picolinafen.
5. The composition of claim 1 containing from 2:1 to 1:2 weight ratio of pyrasulfotole to picolinafen.
6. The composition of claim 1, when applied to a field at a rate to provide from 5 to 50 g/ha of picolinafen to the field.
7. The composition of claim 1, when applied to a field at a rate to provide from 5 to 25 g/ha of picolinafen to the field.
8. The composition of claim 1, when applied to a field at a rate to provide from 5 to 100 g/ha of pyrasulfotole to the field.
9. The composition of claim 1, when applied to a field at a rate to provide from 10 to 75 g/ha of pyrasulfotole to the field.
10. The composition of claim 1, when applied to a field at a rate to provide from 12.5 to 50 g/ha of pyrasulfotole to the field and from 10 to 25 g/ha of picolinafen to the field.
11. The composition of any one of claims 1 to 10 which includes other herbicidally active compounds.
12. The composition of claim 11 wherein the other herbicidally active compounds are selected from chlorsulfuron, imazamox, imazapyr, atrazine, diflufenican, 2,4-dichlorophenoxyacetic acid (2,4-D), dicamba, 2-methyl-4-chlorophenoxyacetic acid (MCPA), bromoxynil, metasulam, flumetsulam, simazine, glyphosate, isoproturon, metribuzin, propanil, glufosinate, clomazone, acetochlor, alachlor, anilofos, flufenacet, metolachlor, thenylchlor flufenacet, mefenacet, mecoprop, dicamba, diflufenzopyr fluroxypyr and quinclorac.
13. The composition of any one of claims 1 to 12 which includes a safener.

14. The composition of claim 13 wherein the safener is selected from mefenpyr-diethyl, oxabetrinil and cloquintocet, and any esters or salts thereof.
15. A method of controlling or suppressing broad-leaved weeds in a field by sequentially or simultaneously applying pyrasulfotole and picolinafen to that field.
16. A method of controlling or suppressing broad-leaved weeds in a field by applying the composition of any one of claim 1 to 14 to the field.
17. The method of claim 15 or 16 when the broad-leaved weeds include wild radish (Raphanus raphanistrum).

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2022/051306

A. CLASSIFICATION OF SUBJECT MATTER

A01N 43/40 (2006.01) A01N 43/56 (2006.01)

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)

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)

PATENW, CAPLUS, CASFORMULTNS, REGISTRY, AGRICOLA, BIOSIS, CABA, CROPU, CROPB, CROPR, GOOGLE PATENTS/SCHOLAR/SEARCH, ESPACENET: IPC/CPC MARKS (A01N, A01P, A01N43/40, A01N43/56) AND KEYWORDS (Pyrasulfotole, Picolinafen, herbicide, wild radish and related terms)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] 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

"D" document cited by the applicant in the international application

"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	Date of mailing of the international search report
7 February 2023	07 February 2023
Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Divya Ramji AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61 2 6283 7954

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2022/051306**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2021/030856 A1 (ADAMA AUSTRALIA PTY LTD) 25 February 2021 Abstract, Example 7, Table 1, Table 14, Claims, page 5 lines 11-15, page 6 line 23-24, page 9 line 5	1-17
A	US 2013/0310257 A1 (ZAGAR et al.) 21 November 2013 Whole Document	1-17
A	US 2014/0309111 A1 (GRIVEAU et al.) 16 October 2014 Whole Document	1-17

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2022/051306**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2022/051306**

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Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
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		WO 2009153246 A2	23 Dec 2009

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.