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(54) Title: HERBICIDAL COMPOSITION

(57) Abstract: The present invention relates to novel herbicidal composition for protecting crops against weeds, undesired vegetation and grasses. More, particularly, the present invention relates to a herbicidal composition comprising a mixture of pyroxasulfone, chlorimuron ethyl and diclosulam. The present invention further relates to a method of controlling weeds comprising applying a composition of the present invention to the weeds or an area in need of weed control.

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HERBICIDAL COMPOSITION

FIELD OF THE INVENTION

[01] The present invention relates to a herbicidal composition for protecting crops against weeds, undesired vegetation and grasses. More, particularly, the present invention relates to a herbicidal composition comprising a mixture of pyroxasulfone, diclosulam and chlorimuron ethyl. The present invention further relates to a method of controlling weeds comprising applying a composition of the present invention to the weeds or an area in need of weed control.

BACKGROUND OF THE INVENTION

[02] Weeds compete with productive crops or pasture, they can be poisonous, distasteful, produce burrs, thorns or otherwise interfere with the use and management of desirable plants by contaminating harvests or interfering with livestock. Weeds compete with crops for space, nutrients, water and light. Smaller, slower growing seedlings are more susceptible than those that are larger and more vigorous. Weeds also vary in their competitive abilities according to conditions and season. Tall-growing vigorous weeds such as fat hen (*Chenopodium album*) can have the most pronounced effects on adjacent crops, although seedlings of fat hen that appear in late summer produce only small plants. Chickweed (*Stellaria media*), a low growing plant, can happily co-exist with a tall crop during the summer, but plants that have overwintered will grow rapidly in early spring and may swamp crops such as onions or spring greens.

[03] The presence of weeds does not necessarily mean that they are damaging a crop, especially during the early growth stages when both weeds and crops can grow without interference. However, as growth proceeds, they begin to require greater amounts of water and nutrients. Estimates suggest that weed and crop can co-exist harmoniously for around three weeks before competition becomes significant.

[04] Several methods of using herbicides to control or eliminate weedy species are known in the art. Chemical herbicides are typically categorized according to the time of application (e.g., pre-emergence or post-emergence herbicides). Pre-emergence herbicides are applied prior to germination of weeds for control of

germinating weed seeds without harming the desired plant species. Post-emergence herbicides are applied after planting and over the top of establishing or established plants for control of unwanted plant species.

[05] Generally, current methods of attempting to control weeds include applications of pre-emergent herbicides followed by post emergent herbicides i.e., sequential applications of herbicides to address the issue of weeds in agricultural crop cultivation. Most of the crop lands under cultivation are weeded by hand, hence, much human effort is expended in raising crops. Most of the times, the dosage used varies as the herbicide selection is not based on the technical knowhow which results in poor weed control affecting the productivity of the crop.

[06] In such usage the chances of varied dosage of individual herbicides end up with poor weed control. Such improper practices also lead to serious complications such as but not limited to increase in population of escape weeds, herbicide tolerance and resistance development, shifting of weed flora etc. However, successful weed management is essential for economical crop production.

[07] To overcome these types of problems, a need arises for the use of pre-mix (ready-mix) herbicidal compositions in which more than one type of herbicide is present in appropriate contents and delivery form i.e., the formulation. It is, nonetheless, difficult to determine appropriate combinations of herbicides in view of the considerable number of different types of herbicides available and the plurality of individual herbicides within each such type.

[08] The herbicidal effectiveness of a compound cannot be predicted from an examination of the substituent groups of the compound and often quite closely related compounds possess different weed control abilities. Various herbicides of the same class of compounds may have complementary areas of activity and thus can be useful to control a variety of weeds upon application of a combination. Furthermore, the various herbicides are not completely effective so as to control all the infesting weeds in a field crop, which necessitates the use of herbicidal combinations. An ideal herbicide should afford selective weed control, over the

full growing season, with a single administration. It should be able to control all common weeds by controlling their growth and reproduction as the seed, the germinating seed, the seedling and the growing weed plant. It is often imperative to use herbicidal combinations to achieve these advantages, although the selection of the components of an ideal combination is not a straightforward choice for a skilled artisan.

[09] It is therefore desired to provide an improved composition and convenient method which safely and effectively control weed species in the agricultural crops and therefore, there is a constant need for the development and application of synergistic formulations which are not only effective in weed control, but also help in increasing the yield of crop, having potential to manage the challenges of resistance development and shifting of weed flora.

SUMMARY OF THE INVENTION

[010] The present invention to provides a herbicidal composition, which allows efficient and reliable control of grass and broadleaf weeds in field with sufficiently long herbicidal activity in order to achieve control of the weeds over a sufficient long time period. The composition of the present invention has low toxicity to humans or other mammals and show an accelerated action on harmful plants, i.e., they should affect damaging of the harmful plants more quickly in comparison with application of the individual herbicides.

[011] The present invention provides a herbicidal composition comprising a mixture of an isooxazoline herbicide, a triazolopyrimidine herbicide, a sulfonylurea herbicide and adjuvants, wherein the isooxazoline herbicide is pyroxasulfone, the triazolopyrimidine herbicide is diclosulam and the sulfonylurea herbicide is chlorimuron ethyl in effective amount and adjuvants.

[012] In an embodiment the present invention, the herbicidal composition comprises a mixture of pyroxasulfone is present in a range from 10% (w/w) to 30% (w/w); diclosulam is present in a range from 1.5% (w/w) to 5% (w/w); and chlorimuron ethyl is present in a range from 0.5% (w/w) to 1.5% (w/w).

[013] In another embodiment of the present invention, the composition comprises the adjuvants selected from a wetting agent, a dispersing agent, a filler, a disintegration agent and a defoamer.

[014] In another embodiment of the present invention, the composition comprise the wetting agent selected from the group comprising dialkyl naphthalene sulphonate sodium salt, alkylnaphthalene sulfonate condensate blend, sodium lauryl sulphate and linear alcohol derivative, present in a range from 2.5% to 5% w/w.

[015] In another embodiment of the present invention, the composition comprises the dispersing agent selected from the group comprising Sodium salt of methyl naphthalene sulfonate, sodium ligno sulphonate, Polyethyleneglycol Nonylphenyl ether ammonium sulfate, acrylate copolymer, phenol sulfonic acid-formaldehyde-polycondensation as sodium salt, sodium polycarboxylate, and sodium methyl oleoyl taurate, or combination thereof, present in a range from 4% to 15% w/w.

[016] In another embodiment of the present invention, the composition comprises the filler selected from the group comprising corn starch, lactose monohydrate, quartz, talc, kaolin, pyrophyllite, montmorillonite, attapulgite, bentonite clay, china clay, kieselguhr, chalk, zeolite, calcite, sericite, acid clay, diatomaceous earth, natural rock, Fuller's earth, meerschaum, gibbsite, dolomite or pumice; synthetic minerals such as precipitated silica, fumed silica, sodium silicate, silicon dioxide, alumina, aluminium silicate, aluminium hydroxide and calcium carbonate, present in a range from 44% to 61% w/w.

[017] In another embodiment of the present invention, the composition comprises the disintegration agent selected from the group comprising ammonium sulphate, sodium tripolyphosphate, sodium salt of naphthalene sulfonate and sodium polycarboxylate, present in an amount of 10% w/w.

[018] In another embodiment of the present invention, the composition comprises the defoamer polydimethyl siloxane, present in a range from 1% to 3% w/w.

[019] In another embodiment of the present invention, the composition is formulated as water dispersible granule.

DESCRIPTION OF THE INVENTION

[020] The following detailed description is presented to enable any person skilled in the art to make and use the invention. For purposes of explanation, specific nomenclature is set forth to provide a thorough understanding of the present application. However, it will be apparent to one skilled in the art that these specific details are not required to practice the invention. Descriptions of specific applications are provided only as representative examples. The present application is not intended to be limited to the embodiments shown but is to be accorded the widest possible scope consistent with the principles and features disclosed herein.

[021] It is to be noted that, as used in the specification, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a composition containing “a compound” includes a mixture of two or more compounds. It should also be noted that the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

[022] Similarly, the words "comprise," "comprises," and "comprising" are to be interpreted inclusively rather than exclusively. Likewise, the terms "include" "including" and "or" should all be construed to be inclusive, unless such a construction is clearly prohibited from the context. However, the embodiments provided by the present disclosure may lack any element that is not specifically disclosed herein. Thus, a disclosure of an embodiment defined using the term "comprising" is also a disclosure of embodiments "consisting essentially of' and "consisting of' the disclosed components. Where used herein, the term "example, "particularly when followed by a listing of terms, is merely exemplary and illustrative, and should not be deemed to be exclusive or comprehensive. Any embodiment disclosed herein can be combined with any other embodiment disclosed herein unless explicitly indicated otherwise.

[023] The term “active ingredient” (a.i.) or “active agent” used herein refers to that component of the composition responsible for control of weeds, undesired vegetation and grasses.

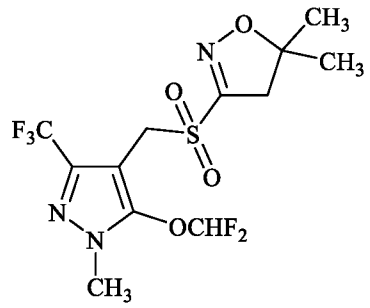
[024] Unless otherwise specified, % refers to % weight; and % weight refers to % of the weight of the respective component with respect to the total weight of the composition.

[025] As used herein, the term "effective amount" means the amount of the active substances in the compositions to achieve an observable effect on growth, including the effects of necrosis, death, retardation, prevention, and removal, destruction, or otherwise diminishing the occurrence and activity of the target weed. The effective amount can vary for the various compositions used in the present invention. An effective amount of the compositions will also vary according to the prevailing conditions such as desired herbicidal effect and duration, weather, target species, locus, mode of application, and the like. The terms plants, weeds and vegetation include germinant seeds, emerging seedlings, plants emerging from vegetative propagules and established vegetation.

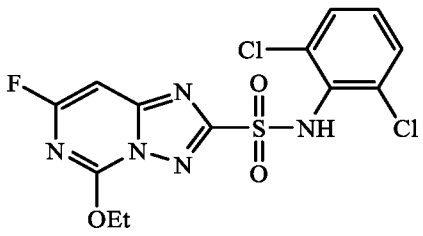
[026] As used herein, “controlling undesirable vegetation” means preventing, reducing, killing, or otherwise adversely modifying the development of plants and vegetation. Described herein are methods of controlling undesirable vegetation through the application of certain herbicide combinations or compositions. Methods of application include, but are not limited to applications to the vegetation or locus thereof, e.g., application to the area adjacent to the vegetation, as well as pre-emergence, post-emergence, foliar (broadcast, directed, banded, spot, mechanical, over-the-top, or rescue), and in-water applications (emerged and submerged vegetation, broadcast, spot, mechanical, water-injected, granular broadcast, granular spot, shaker bottle or stream spray) via hand, backpack, machine, tractor, or aerial application methods.

[027] Pyroxasulfone, chemically known as 3-[5-(difluoromethoxy)-1-methyl-3-(trifluoromethyl) pyrazol-4-ylmethylsulfonyl]-4,5-dihydro-5,5-dimethyl-1,2-oxazole, is relatively new isooxazoline herbicide that inhibits synthesis of very -long- chain fatty acids. The structure of the existing herbicide thiobencarb served as the basis for development but pyroxasulfone requires a lower dose (100–25 g/ha) and is more stable resulting in longer efficacy. Pyroxasulfone is used to control weeds among many agricultural crops including corn and soybean. This

herbicide is a different chemistry class – it is an isoxazoline. This means that pyroxasulfone brings more activity to a broader spectrum of small-seeded plants than other, older chemicals. Pyroxasulfone binds with clay in the soil which can make it more effective against weeds for longer. The chemical structure of Pyroxasulfone is

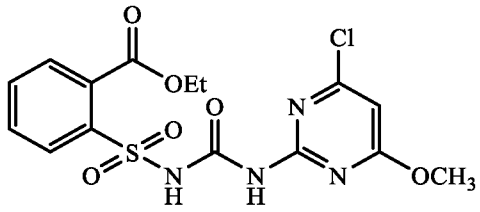


[028] Diclosulam, chemically known as [N-(2,6-dichlorophenyl)-5-ethoxy-7-fluoro-(1,2,4)triazolo(1,5-c)pyrimidine-2-sulphonamide], belonging to the sulfonanilide triazolopyrimidine group, whose mechanism of action is the inhibition of acetolactate synthase (ALS), a key enzyme in branched chain amino acid biosynthesis of plants. Diclosulam is a soil applied herbicide. It has a low aqueous solubility, is non-volatile and, based on its chemical properties, is mobile and may leach to groundwater. It tends to be moderately persistent in soil systems. The structure of diclosulam is



[029] Chlorimuron ethyl, chemically known as [ethyl 2-(4-chloro-6-methoxypyrimidin-2-ylcarbamoylsulfmoyl) benzoate] is a sulfonylurea herbicide. Sulfonylurea herbicides function by interfering with the bio-synthesis of amino acids including valine, isoleucine and leucine. Chlorimuron ethyl is used to control weeds among agricultural crops including grains. Chlorimuron-ethyl is a post-emergence, foliar applied herbicide. It has high aqueous solubility, is non-volatile and, based on its chemical properties, is mobile and can be expected to

leach to groundwater. It can be moderately persistent in soil systems but will not usually persist in aquatic systems. The chemical structure of chlorimuron ethyl is



[030] In an embodiment of the invention, the herbicidal composition comprises of Pyroxasulfone present in a range from 10% to 30% (w/w), Diclosulam is present in a range from 1.5% to 5% (w/w), Chlorimuron ethyl is present in a range from 0.5% to 1.5% (w/w), and suitable adjuvants.

[031] The herbicidal composition in addition to herbicidal actives further contains a support, an adjuvant and/or a surfactant. During application, a common adjuvant can be mixed with the composition.

[032] The active compounds within the herbicidal composition according to the invention have potent weedicide activity and can be employed for controlling undesired weeds, vegetation and sedges.

[033] Suitable adjuvants may be a solid or liquid and are generally a substance commonly used in formulation processing process, for example, wetting agent, dispersing agent, filler, disintegrating agent and defoamer.

[034] In an embodiment of the invention the herbicidal composition of the present invention may further be mixed with other herbicidal active ingredients, whereby the spectrum of weeds to be controlled, the application timing, the herbicidal activity, etc. can be improved to preferred directions in some cases.

[035] The novel herbicidal composition of the present invention may be formulated as Granular composition (GR), Capsule suspension (CS), Dispersible concentrate (DC), Dustable powder (DP), Powder for dry seed treatment (DS), Emulsifiable concentrate (EC), Emulsifiable granule (EG), Emulsion water-in-oil (EO), Emulsifiable powder (EP), Emulsion for seed treatment (ES), Emulsion oil-in-water (EW), Flowable concentrate for seed treatment (FS), Granules (GR), Micro-emulsion (ME), Oil-dispersion (OD), Oil miscible flowable concentrate (OF), Oil miscible liquid (OL), Oil dispersible powder (OP), Suspension

concentrate (SC), Suspension concentrate for direct application (SD), Suspo-emulsion (SE), Water soluble granule (SG), Soluble concentrate (SL), Spreading oil (SO), Water soluble powder (SP), Water soluble tablet (ST), Ultra-low volume (ULV) suspension, Tablet (TB), Ultra-low volume (ULV) liquid, Water dispersible granules (WG), Wettable powder (WP), Water dispersible powder for slurry seed treatment (WS), Water dispersible tablet (WT), a mixed formulation of CS and SC (ZC), a mixed formulation of CS and SE (ZE), a mixed formulation of CS and EW (ZW). Preferably, the composition of the present invention is in form of water dispersible granule (WDG).

[036] Wetting is the first stage of dispersion, in which the air surrounding the granular composition is substituted with water. Wetting of the herbicidal composition with water cannot occur if the surface tension of the liquid is very high. Hence, it is recommended to add a wetting agent to the herbicidal composition to facilitate the process of dispersion of the granules in the liquid. Accordingly, the composition of the present invention preferably contains a wetting agent such as naphthalene alkyl aryl sulphonate, dioctyl sulfosuccinate, sodium lauryl sulfate, non-ionic ethoxylated polyarylphenol phosphate ester, sodium alkyl naphthalene sulfonate or a combination thereof. Preferably, the wetting agent suitable for use in the present invention are dialkyl naphthalene sulphonate sodium salt, alkylnaphthalene sulfonate condensate blend, sodium lauryl sulphate and linear alcohol derivative. Wetting agent is present in a range from 2.5% to 5% (w/w) in the compositions of the present invention.

[037] It is generally observed that solid particles in a liquid undergo spontaneous aggregation to form lumps. Hence it is recommended to add a dispersant or a dispersing agent which prevents aggregation of solid particles and keeps them suspended in the fluid. Accordingly, the composition of the present invention preferably contains a dispersing agent such as amine salt of phosphate tristyryl phenol ethoxylated, acrylic copolymer, naphthalene sulphonate of formaldehyde condensate, lignin based sulphonate. One or more dispersing agents may be used in the synergistic composition of the present invention. The dispersing agent suitable for use in the present invention are Sodium salt of methyl naphthalene sulfonate, sodium ligno sulphonate, Polyethyleneglycol Nonylphenyl ether

ammonium sulfate, acrylate copolymer, phenol sulfonic acid-formaldehyde-polycondensation as sodium salt, sodium polycarboxylate, sodium methyl oleoyl taurate and sodium lauryl sulphate or combination thereof. Dispersing agent is present in a range from 4% to 15% (w/w) in the compositions of the present invention.

[038] A "filler" refers to solid chemicals that are added to an herbicide formulation to aid in the delivery of the active ingredient. Filler is selected from the group comprising of, but not limited to, natural minerals such as corn starch, lactose monohydrate, quartz, talc, kaolin, pyrophyllite, montmorillonite, attapulgite, bentonite clay, china clay, kieselguhr, chalk, zeolite, calcite, sericite, acid clay, diatomaceous earth, natural rock, Fuller's earth, meerschaum, gibbsite, dolomite or pumice; synthetic minerals such as precipitated silica, fumed silica, sodium silicate, silicon dioxide, alumina, aluminium silicate, aluminium hydroxide; inorganic salts such as calcium carbonate, ammonium salts, sodium sulfate, potassium chloride. The filler may be used alone or in combination thereof. Preferably, the filler suitable for use in the present invention are lactose monohydrate, calcium carbonate, china clay. Filler is present in a range from 44% to 61% (w/w).

[039] Disintegrating agent are additive that can be some time useful for improving dispersibility of herbicide formulation. The disintegrating agent suitable for the purpose of the present invention is selected from the group comprising ammonium sulphate, sodium tripolyphosphate, sodium salt of naphthalene sulfonate and sodium polycarboxylate. The disintegrating agent is present in an amount of 10% (w/w).

[040] Defoamer is a chemical reagent developed for defoaming and foam suppression based on the principle of foaming. The defoamer suitable for the purpose of the present invention is polydimethyl siloxane. The defoamer is present in a range from 1% to 3% (w/w).

[041] The synergistic herbicidal composition of the present invention was found to be non-phytotoxic and has good stability, wettability, suspensibility and dispersibility.

[042] In an embodiment of the invention the herbicidal composition of the present invention may be applied to undesired plants, weeds or may be applied to a place where they grow. Further, it may be applied at any time either before or after the emergence of the undesired plants or weeds. Further, the herbicidal composition of the present invention may be applied in different application forms such as soil application, foliar application, irrigation application, and submerged application, and it can be applied to agricultural fields such as upland fields, orchards and paddy fields, and non-cropland such as ridges of fields, fallow fields, playgrounds, golf courses, vacant lands, forests, factory sites, railway sides and roadsides.

[043] In an embodiment of the invention, the composition comprises a combination of herbicides differing in the mode of action, it can control weeds having decreased sensitivity to many herbicides.

[044] In an embodiment of the invention, the herbicidal composition of the present invention may be mixed with or may be used in combination with other herbicides, fungicides, antibiotics, plant hormones, insecticides, fertilizers, phytotoxicity-reducing agents, etc., in addition to the above active ingredients, without departing from the intention and the scope of the present invention, whereby more excellent effects and activities may sometimes be obtained.

[045] The herbicidal composition according to the invention can be applied before and after the plants have emerged, that is to say pre-emergence and post-emergence. It can also be incorporated into the soil before sowing. The good herbicidal activity of the herbicidal composition of the present invention can be seen from the examples which follow. While the individual active compounds show weak points regarding the herbicidal activity, the combinations, without exception, display a very good activity against weeds, which exceeds a simple additive effect. A synergistic effect in herbicides is always present when the herbicidal activity of the active combination exceeds the activity of the active compounds when applied individually.

[046] The present invention is more particularly described in the following examples that are intended as illustrations only, since numerous modifications and variations within the scope of the present invention will be apparent to those of

skill in the art. Unless otherwise noted, all parts, percentages, and ratios reported in the following examples are on a weight basis and all reagent used in the example were obtained or are available from the chemical suppliers.

[047] Examples:

[048] Example 1: Preparation of composition of Pyroxasulfone, Diclosulam and Chlorimuron ethyl in Water Dispersible Granule form (WDG)

[049] Step 1: weighing the raw materials according to the batch size as follows:

a. filler
b. dispersing agent
c. wetting agent
d. Pyroxasulfone
e. Diclosulam
f. Chlorimuron ethyl
g. disintegrating agent
h. defoamer

weighing all this raw material in a pre-blender and mixing it for 1 hr;

Step 2: Milling the sample through air jet mill instrument at Inlet pressure 2-3 kg/cm^{2,} grinding pressure 6 kg/ cm^2 and checking the particle size < 12 micron;

Step 3: Collecting the milled material, and post blending the sample for 1 hr;

Step 4: Extruding the granule @35 rpm (1.0 mesh);

Step 5: Collecting the granules and dry the sample at 45 °C for 30 min;

Step 6: Sending the sample to the Quality analysis;

Step 7: Packing the formulated material in a suitable packaging.

[050] Example 2: Compositions of the present invention

The illustrative embodiments show the composition of Pyroxasulfone, Diclosulam, and Chlorimuron ethyl in water dispersible granule form in different amount as follows:

[051] Table 1: Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG

S. No.	Compositions	Function	%(w/w)
1.	Pyroxasulfone	Active ingredient	30.0
2.	Diclosulam	Active ingredient	5.0
3.	Chlorimuron ethyl	Active ingredient	1.5
4.	Dialkyl naphthalene sulphonate sodium salt	Wetting agent	2.5
5.	Sodium Ligno sulfonate	Dispersing agent	6.0
6.	Corn Starch	Filler	33.0
7.	China clay	Filler	11.0
8.	Ammonium Sulphate	Disintegrating agent	10.0
9.	Polydimethylsiloxane	Defoamer	1.0
Total			100

[052] The process for manufacture of composition of Table 1 is as follows: 30.0 gm of pyroxasulfone, 5.0 gm of diclosulam, 1.5 gm of chlorimuron ethyl, 2.5 gm of dialkyl naphthalene sulphonate sodium salt, 6.0 gm of sodium ligno sulfonate, 33.0 gm of corn starch, 11.0 gm of china clay, 10.0 gm of ammonium sulphate, and 1.0 gm of polydimethylsiloxane were weighed in the pre-blender reactor and mixed for 1 hour. The mixture was milled through air jet mill instrument (Inlet pressure 2-3 kg/cm^2, grinding pressure 6 kg/ cm^2) to obtain the desired particle size (D_{90} < 12 microns). Collecting the milled material and post blending the material for 1 hour. Extruding the granule at 35 rpm (1.0 mesh), collecting the granules and drying at 45 °C for 30 min followed by packing the material in a suitable package.

[053] Table 2: Pyroxasulfone 15% + Diclosulam 1.5% + Chlorimuron ethyl 0.5% WDG

S. No.	Compositions	Function	%(w/w)

1.	Pyroxasulfone	Active ingredient	15.0
2.	Diclosulam	Active ingredient	1.5
3.	Chlorimuron ethyl	Active ingredient	0.5
4.	Alkylnaphthalene sulfonate condensate blend	Wetting agent	5.0
5.	Phenol sulfonic acid-formaldehyde-polycondensation as sodium salt	Dispersing agent	3.0
6.	Acrylate copolymer	Dispersing agent	1.0
7.	Ammonium sulphate	Disintegrating agent	10.0
8.	Polydimethylsiloxane	Defoamer	3.0
9.	China clay	Filler	61.0
Total			100

[054] The process for manufacture of composition of Table 2 is as follows: 15.0 gm of pyroxasulfone, 1.5 gm of diclosulam, 0.5 gm of chlorimuron ethyl, 5.0 gm of Alkylnaphthalene sulfonate condensate blend, 3.0 gm of phenol sulfonic acid-formaldehyde-polycondensation as sodium salt, 1.0 gm of acrylate copolymer, 10.0 gm of ammonium sulphate, 3.0 gm of polydimethylsiloxane, and 61.0 gm of china clay were weighed in the pre-blender reactor and mixed for 1 hour. The mixture was milled through air jet mill instrument (Inlet pressure 2-3 kg/cm^2, grinding pressure 6 kg/ cm^2) to obtain the desired particle size (D_{90} < 12 microns). Collecting the milled material and post blending the material for 1 hour. Extruding the granule at 35 rpm (1.0 mesh), collecting the granules and drying at 45^{o}C for 30 min followed by packing the material in a suitable package.

[055] Table 3: Pyroxasulfone 20% + Diclosulam 2% + Chlorimuron ethyl 5% WDG

S. No.	Compositions	Function	%(w/w)

1.	Pyroxasulfone	Active ingredient	20.0
2.	Diclosulam	Active ingredient	2.0
3.	Chlorimuron ethyl	Active ingredient	1.0
4.	Dialkyl naphthalene sulphonate sodium salt	Wetting agent	5.0
5.	Sodium salt of methyl naphthalene sulfonate	Dispersing agent	10.0
6.	Phenol sulfonic acid-formaldehyde-polycondensation as sodium salt	Dispersing agent	5.0
7.	Ammonium sulphate	Disintegrating Agent	10.0
8.	Polydimethylsiloxane	Defoamer	1.0
9.	Calcium carbonate	Filler	46.0
Total			100

[056] The process for manufacture of composition of Table 3 is as follows: 20.0 gm of pyroxasulfone, 2.0 gm of diclosulam, 1.0 gm of chlorimuron ethyl, 5.0 gm of Dialkyl naphthalene sulphonate sodium salt, 10.0 gm of Sodium salt of methyl naphthalene sulfonate, 5.0 gm of Phenol sulfonic acid-formaldehyde-polycondensation as sodium salt, 10.0 gm of ammonium sulphate, 1.0 gm of polydimethylsiloxane, and 46.0 gm of calcium carbonate were weighed in the pre-blender reactor and mixed for 1 hour. The mixture was milled through air jet mill instrument (Inlet pressure 2-3 kg/cm2, grinding pressure 6 kg/ cm2) to obtain the desired particle size (D90 < 12 microns). Collecting the milled material and post blending the material for 1 hour. Extruding the granule at 35 rpm (1.0 mesh), collecting the granules and dry at 45 °C for 30 min followed by packing the material in a suitable package.

[057] Table 4: Pyroxasulfone 25% + Diclosulam 3% + Chlorimuron ethyl 1.3% WDG

S. No.	Compositions	Function	%(w/w)
1.	Pyroxasulfone	Active ingredient	25.0
2.	Diclosulam	Active ingredient	3.0
3.	Chlorimuron ethyl	Active ingredient	1.3
4.	Linear Alcohol Derivative	Wetting agent	4.5
5.	Sodium polycarboxylate	Dispersing agent	2.5
6.	Sodium Methyl Oleoyl Taurate	Dispersing agent	3.0
7.	Polydimethylsiloxane	Defoamer	2.5
8.	Ammonium sulphate	Disintegrating Agent	10.0
9.	Calcium carbonate	Filler	48.2
Total			100

[058] The process for manufacture of composition of Table 4 is as follows: 25.0 gm of pyroxasulfone, 3.0 gm of diclosulam, 1.3 gm of chlorimuron ethyl, 4.5 gm of Linear Alcohol Derivative, 2.5 gm of Sodium polycarboxylate, 3.0 gm of Sodium Methyl Oleoyl Taurate, 2.5 gm of polydimethylsiloxane, 10.0 gm of ammonium sulphate, and 48.2 gm of calcium carbonate were weighed in the pre-blender reactor and mixed for 1 hour. The mixture was milled through air jet mill instrument (Inlet pressure 2-3 kg/cm2, grinding pressure 6 kg/ cm2) to obtain the desired particle size (D90 < 12 microns). Collecting the milled material and post blending the material for 1 hour. Extruding the granule at 35 rpm (1.0 mesh), collecting the granules and dry at 45 °C for 30 min followed by packing the material in a suitable package.

[059] Table 5: Pyroxasulfone 10% + Diclosulam 4% + Chlorimuron ethyl 0.8% WDG

S. No.	Compositions	Function	%(w/w)
1	Pyroxasulfone	Active ingredient	10.0

2	Diclosulam	Active ingredient	4.0
3	Chlorimuron ethyl	Active ingredient	0.8
4	Polyethyleneglycol Nonylphenyl ether ammonium sulfate	Dispersing agent	5.0
5	Sodium Ligno sulphonate	Dispersing agent	10.0
6	Sodium lauryl sulphate	Wetting agent	5.0
7	Ammonium Sulphate	Disintegrating agent	10.0
8	Lactose Monohydrate	Filler	55.2
Total			100

[060] The process for manufacture of composition of Table 5 is as follows: 10.0 gm of pyroxasulfone, 4.0 gm of diclosulam, 0.8 gm of chlorimuron ethyl, 5.0 gm of Polyethyleneglycol Nonylphenyl ether ammonium sulfate, 10.0 gm of Sodium Ligno sulphonate, 5.0 gm of Sodium lauryl sulphate, 10.0 gm of ammonium sulphate, and 55.2 gm of Lactose Monohydrate were weighed in the pre-blender reactor and mixed for 1 hour. The mixture was milled through air jet mill instrument (Inlet pressure 2-3 kg/cm2, grinding pressure 6 kg/ cm2) to obtain the desired particle size (D90 < 12 microns). Collecting the milled material and post blending the material for 1 hour. Extruding the granule at 35 rpm (1.0 mesh), collecting the granules and dry at 45˚C for 30 min followed by packing the material in a suitable package.

[061] Example 4: Bio-efficacy study of combination of Pyroxasulfone, Diclosulam and Chlorimuron ethyl

FIELD AND SYNERGY STUDIES

[062] Soybean is an important rainy season crop of India. In India, it is grown on an area of 108.83 lakh ha with an annual production of 104.36 lakh million

tonnes. Successful weed control is most important factor for fruitful soybean production because losses due to weeds have been one of the major limiting factors in soybean production. Weeds compete with crop for light, moisture and nutrients. Being a rainy season crop soybean faces severe weed competition during crop growth, resulting in a loss of about 40-60% of the potential yield. Traditionally, weed control in India has been largely dependent on manual weeding. However, increased labour scarcity and costs are encouraging farmers to adopt to use herbicides.

[063] The field studies were conducted to compare the weed controlling activity of the combination of Pyroxasulfone, Diclosulam and Chlorimuron ethyl. The active ingredient Pyroxasulfone in the combination, belongs to chemical family "Isooxazolines" with mode of action of inhibition of very long chain fatty acids synthesis (VLCFA) inhibitors and Diclosulam belongs to chemical family "Triazolopyrimidine" with Acetolactate synthase (ALS inhibitor) mode of action whereas, Chlorimuron ethyl is belonging to chemical family "Sulfonylureas" with ALS inhibitor (inhibition of acetolactate synthase) mode of action. This combination helps in controlling the cross-spectrum weeds (broad leaf weeds, grassy weeds, and sedges) in soybean when applied in pre-emergence (0-2 DAS) application timing. All the molecules are safe to soybean.

[064] The weed control activity of the individual herbicides of the invention and their combinations were evaluated on weeds such as *Acalypha indica, Commelina benghalensis, Commelina communis, Digera arvensis, Echinochloa colona* and *Dinebra retroflexa*. Trials were conducted with randomized block design with net plot size of 5m x 6m. Each trial was replicated four times and conducted under GEP guidelines. Spraying was done with manual operated backpack knapsack sprayer with 300 L of water spray volume per hectare at pre-emergence (0-2 DAS) application timing. Such field trials were carried out at various locations to generate independent data, the locations were chosen randomly across India.

[065] Visual observations were recorded on percent weed control for individual weeds on whole plot basis at 30 days after application. These observations are to be taken from entire plot.

[066] Appropriate analysis of plant response to herbicide combination is critical in determining the type of activity observed. The most widely used model is one Gowing* derived and Colby** modified. Gowing described a mathematical formula for calculating the predicting response values for pesticide mixtures. He suggested the expected (E) percent inhibition of growth induced by pesticide A plus pesticide B and plus pesticide C is as follows, *(Jerry Flint *et al,* 1988) ***

$$\text{Expected (E)} = A + B + C - \frac{(AB + AC + BC)}{100} + \frac{ABC}{10000}$$

Where,

A = observed efficacy of active ingredient A at the same concentration as used in the mixture.

B = observed efficacy of active ingredient B at the same concentration as used in the mixture.

C = observed efficacy of active ingredient C at the same concentration as used in the mixture.

When the percentage of pesticidal control observed for the combination is greater than the expected percentage, there is a synergistic effect. (Ratio of O/E > 1, means synergism observed.)

Reference:

*Gowing, D. P. 1960. Comments on tests of herbicide mixtures. Weeds 8:379–391.

**Colby, S. R. 1967. Calculating synergistic and antagonistic responses of herbicide combinations. Weeds 15:20–22

*** Jerry Flint et al, 1988. Analyzing Herbicide Interactions: A Statistical Treatment of Colby's Method. Weed Technology 2: 304-309

[067] The herbicide combinations, application rates, plant species tested, and results are given in the following tables:

[068] **Table 6:** Table 6 demonstrates synergy on weeds using the combination of Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG. The field trials were carried out in India at various locations. The percentage efficacy was calculated after 30 days of application. The target weeds were ***Commelina benghalensis*** and ***Commelina communis*** and the results are recorded in the table 6 below.

Active	**Dose (GAH)**	**% Weed Control of *Commelina benghalensis***		**% Weed Control of *Commelina communis***	
		Expected	**Observed**	**Expected**	**Observed**
Pyroxasulfone	120		15		10
Diclosulam	20		60		55
Chlorimuron ethyl	6		45		30
Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG	120 + 20 + 6	81.3	85	71.65	80
Ratio of O/E		**1.05**		**1.12**	

WDG – Water dispersible granules and GAH- gram active per hectare.

[069] The results in table 6 clearly demonstrates synergy between Pyroxasulfone, Diclosulam and Chlorimuron ethyl against weeds like, ***Commelina benghalensis*** and ***Commelina communis***. The higher ratio of the observed and the expected efficacy clearly demonstrates the synergistic effect of the combination.

[070] **Table 7:** Table 7 demonstrates synergy on weeds using the combination of Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG. The field trials were carried out in India at various locations. The percentage efficacy was calculated after 30 days of application. The target weeds were ***Acalypha indica*** and ***Digera arvensis*** and the results are recorded in the table 7 below.

Active	Dose (GAH)	% Weed Control of *Acalypha indica*		% Weed Control of *Digera arvensis*	
		Expected	Observed	Expected	Observed
Pyroxasulfone	120		10		60
Diclosulam	20		75		65
Chlorimuron ethyl	6		30		40
Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG	120 + 20 + 6	84.25	90	91.6	98
Ratio of O/E		**1.07**		**1.07**	

WDG – Water dispersible granules and GAH- gram active per hectare.

[071] The results in table 7 clearly demonstrates efficacy Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG against weeds like, ***Acalypha indica*** and ***Digera arvensis***. The higher ratio of the observed and the expected efficacy clearly demonstrates the synergistic effect of the combination.

[072] **Table 8:** Table 8 demonstrates synergy on weeds using the combination of Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG. The field trials were carried out in India at various locations. The percentage efficacy was calculated after 30 days of application. The target weeds were ***Echinochloa colona*** and ***Dinebra retroflexa*** and the results are recorded in the table 8 below.

Active	Dose (GAH)	% Weed Control of *Echinochloa colona*		% Weed Control of *Dinebra retroflexa*	
		Expected	Observed	Expected	Observed
Pyroxasulfone	120		60		70
Diclosulam	20		65		70

Chlorimuron ethyl	6		10		20
Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG	120 + 20 + 6	87.4	90	92.8	98
Ratio of O/E		**1.03**		**1.06**	

WDG – Water dispersible granules and GAH- gram active per hectare.

[073] The results in table 8 clearly demonstrates efficacy of Pyroxasulfone 30% + Diclosulam 5% + Chlorimuron ethyl 1.5% WDG against weeds like ***Echinochloa colona*** and ***Dinebra retroflexa***. The higher ratio of the observed and the expected efficacy clearly demonstrates the synergistic effect of the combination.

[074] The herbicidal composition of the present invention is capable of controlling a wide range of undesired plants emerging in agricultural fields or non-agricultural fields. It has a remarkable herbicidal activity when a composition comprising Pyroxasulfone and Diclosulam, and Chlorimuron ethyl as a specific third herbicidally active ingredient are used in combination. It represents a synergistic effect i.e., a herbicidal effect higher than the mere addition of the herbicidal effect of the combination of Pyroxasulfone and Diclosulam and the herbicidal effect of the third herbicidally active ingredient.

[075] That is, the herbicidal composition of the present invention can be applied at a low dose as compared with a case where the respective active ingredients are applied individually. Thus, it is effective to reduce the environmental load on an area where the composition is applied or a surrounding area thereof.

[076] From the foregoing it will be observed that numerous modifications and variations can be effectuated without departing from the scope of the novel concepts of the present invention. It is to be understood that no limitations with respect to the specific embodiments illustrated is intended or should be inferred. It should be understood that all such modifications and improvements have been

deleted herein for the sake of conciseness and readability but are properly within the scope of the following claims.

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We claim:

1. An herbicidal composition comprising a mixture of an isooxazoline herbicide, a triazolopyrimidine herbicide, a sulfonylurea herbicide and adjuvants.
2. The herbicidal composition as claimed in claim 1, wherein the isooxazoline herbicide is pyroxasulfone, the triazolopyrimidine herbicide is diclosulam and the sulfonylurea herbicide is chlorimuron ethyl in effective amount and adjuvants.
3. The herbicidal composition as claimed in claim 2, wherein the pyroxasulfone is present in a range from 10% (w/w) to 30% (w/w); diclosulam is present in a range from 1.5% (w/w) to 5% (w/w) and chlorimuron ethyl is present in a range from 0.5% (w/w) to 1.5% (w/w).
4. The herbicidal composition as claimed in claim 1, wherein the adjuvants are selected from a wetting agent, a dispersing agent, a filler, a disintegration agent and a defoamer.
5. The herbicidal composition as claimed in claim 4, wherein the wetting agent is selected from the group comprising dialkyl naphthalene sulphonate sodium salt, alkylnaphthalene sulfonate condensate blend, sodium lauryl sulphate and linear alcohol derivative, present in a range from 2.5% to 5% w/w.
6. The herbicidal composition as claimed in claim 4, wherein the dispersing agent is selected from the group comprising Sodium salt of methyl naphthalene sulfonate, sodium ligno sulphonate, Polyethyleneglycol Nonylphenyl ether ammonium sulfate, acrylate copolymer, phenol sulfonic acid-formaldehyde-polycondensation as sodium salt, sodium polycarboxylate, and sodium methyl oleoyl taurate or combination thereof, present in a range from 4% to 15% w/w.
7. The herbicidal composition as claimed in claim 4, wherein the filler is selected from the group comprising corn starch, lactose monohydrate, quartz, talc, kaolin, pyrophyllite, montmorillonite, attapulgite, bentonite clay, china clay, kieselguhr, chalk, zeolite, calcite, sericite, acid clay, diatomaceous earth, natural rock, Fuller's earth, meerschaum, gibbsite, dolomite or pumice; synthetic minerals such as precipitated silica, fumed silica, sodium silicate,

silicon dioxide, alumina, aluminium silicate, aluminium hydroxide and calcium carbonate, present in a range from 44% to 61% w/w.

8. The herbicidal composition as claimed in claim 4, wherein the disintegration agent is selected from the group comprising ammonium sulphate, sodium tripolyphosphate, sodium salt of naphthalene sulfonate and sodium polycarboxylate present in an amount of 10% w/w.
9. The herbicidal composition as claimed in claim 4, wherein the defoamer is polydimethyl siloxane, present in a range from 1% to 3% w/w.
10. The herbicidal composition as claimed in claim 1, wherein the composition is formulated as water dispersible granule.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2022/050962

A. CLASSIFICATION OF SUBJECT MATTER
A01N47/36,A61K31/64,A01N43/00 Version=2023.01

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)

A01N, A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

PatSeer, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	CA2716674A1 (BASF SE [DE]) 17 SEPTEMBER 2009 (17-09-2009) para [0028]-[0029], claim 1, abstract, formulation F	1-10
Y	US2019045788A1 (VALENT USA CORP [US]) 14 FEBRUARY 2019 (14-02-2019) abstract, claims 1-18	1-10
Y	WO2004080173A2 (BASF AG [DE]) 23 SEPTEMBER 2004 (23-09-2004) claims 1-17	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14-02-2023	14-02-2023
Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Authorized officer Preeti Bansal Telephone No. +91-1125300200

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2022/050962

Citation	Pub.Date	Family	Pub.Date
CA 2716674 A1	17-09-2009	WO 2009112454 A3	20-05-2010
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