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(54) Title: NOVEL HERBICIDAL COMBINATION

(57) Abstract: The present invention relates to a novel herbicidal composition comprising of (a) triazinyl sulfonylurea (b) synthetic auxin and (c) a phenyl pyrazoline. Particularly the present invention relates to a synergistic herbicidal composition comprising the triazinyl sulfonyl urea herbicide is metsulfuron methyl, the synthetic auxin is fluroxypyr meptyl and phenyl pyrazoline is pinoxaden in synergistically effective amounts which is suitable for preventing unwanted plants in wheat crops.

NOVEL HERBICIDAL COMBINATION

FIELD OF THE INVENTION

The present invention relates to a novel herbicidal composition comprising of (a) triazinyl sulfonylurea (b) synthetic auxin and (c) a phenyl pyrazoline. Particularly the present invention relates to a synergistic herbicidal composition comprising the triazinyl sulfonyl urea herbicide is metsulfuron methyl, the synthetic auxin is fluroxypyr meptyl and phenyl pyrazoline is pinoxaden in synergistically effective amounts which is suitable for preventing unwanted plants in wheat crops.

More particularly the present invention provides a method for controlling undesired plants or inhibiting their growth, which comprises applying a herbicidally effective amount of the said composition to the undesired plants or to a place where they grow.

BACKGROUND OF THE INVENTION

Herbicides are the most used method in our country and worldwide for the control of weed due to easy application, getting the results in a short time, having long lasting and powerful effect. They have nowadays increasingly become the most important and indispensable control method in agricultural production. They are used for a long time to increase the production of agricultural activities.

But the continued use of herbicides created many problems like weed resistance, shift weed in shift flora, and environment hazards. From this all-problems herbicide resistance is very serious problem in present time all over the world. The main reasons for resistance are lack of rotation of the herbicide and use of herbicides with long residue period. Herbicide resistance is a worldwide phenomenon and the number of resistant biotypes of weeds is increasing at an alarming rate. Currently there are 480 cases of herbicide resistance in 252 plant species. Herbicide resistance in weeds should be minimized because it is a major limiting factor of food security. A proper knowledge of development and mechanism of resistance would help us with its management.

Herbicide resistance problems are controlled with integrated weed management practices, including crop and herbicide rotations, herbicide combinations, and cultural, mechanical, and biological methods of weed control.

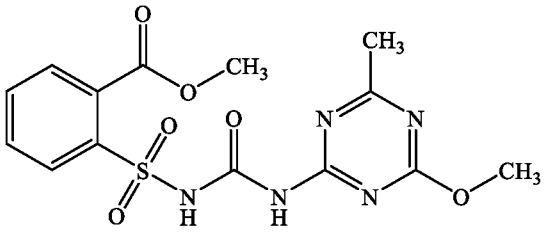
Hence, there is always a need for new active ingredients or new combinations of existing active ingredients to overcome the existing problems faced in the agricultural industry.

Compositions comprising a single herbicidally active component suffer from numerous drawbacks such as formation of resistant weeds, requirement of high amount and concentration of the active ingredient, environmental damage, seepage of the active component into ground water, phytotoxicity and harmful effects on the health of animals and humans.

Active compounds having different mechanisms of action are combined to delay the generation of resistance and reduce the amount of application and prevention and treatment costs. Consequently, research is being conducted to produce herbicides and combinations of herbicides that are safer, that have better performance, that require lower dosages, that are easier to use, and that cost less.

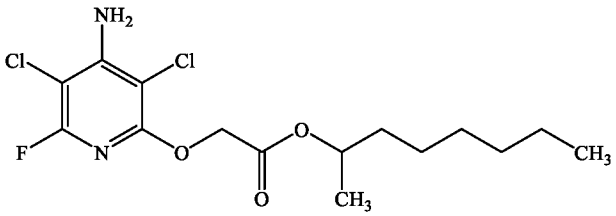
Metsulfuron-methyl is an organic compound classified as a sulfonylurea herbicide, which kills broadleaf weeds and some annual grasses. It is a pre-emergence and post-emergence herbicide used to control annual grasses, brushes, woody plants, and broadleaf weeds. It can be applied to cereals including barley, rye, and wheat and to pastures. It is primarily used to control brush, woody plants and broadleaf weeds on rights-of-way, fence rows, storage areas, highways, and other non-crop areas.

Metsulfuron methyl is chemically known as methyl 2-(N-((4-methoxy-6-methyl-1,3,5-triazin-2-yl) carbamoyl) sulfamoyl) benzoate that inhibits the acetolactate synthase (ALS) in plants as described in US 4394506 and has the following structure:



Fluroxypyr meptyl is a post-emergence herbicide used to control economically important broad-leaved weeds including kochia, lespedeza and dog fennel, woody brush among others.

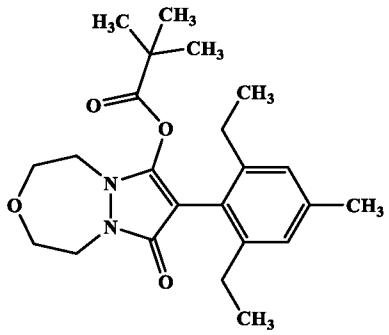
Fluroxypyr meptyl is chemically known as ((4-Amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy)-acetic acid 1-methylheptyl ester. It is described in US3761486 and has the following structure:



Pinoxaden is a representative of the new phenyl pyrazoline class of chemicals, which is a highly selective systemic herbicide used to control monocotyledonous grass weeds in crops such as wild oats, rye grass and black grass in winter and spring wheat and winter and spring barley. Pinoxaden is developed by Syngenta and is used against grasses. The effect is based on influencing the lipid metabolism of the cells. It inhibits acetyl-CoA carboxylase.

Pinoxaden is approved for post emergence control of grass weeds in wheat (including durum) and barley. One application per crop season by agricultural workers using either open-cab ground boom equipment or via aerial application.

Pinoxaden is chemically known as 8-(2,6-Diethyl-p-tolyl)-1,2,4,5-tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepine-9-yl-2,2-dimethylpropionate and is described in US6410480. It has the following chemical structure:



The synergistic herbicidal composition of the present invention can control a wide range of undesired plants emerging in agricultural fields or non-agricultural fields. It has a remarkable herbicidal activity when a composition comprising Metsulfuron methyl, Fluroxypyr meptyl, and Pinoxaden are used in combination.

OBJECT OF THE INVENTION

In one object of the present invention is to provide a novel herbicidal composition comprising of (a) triazinyl sulfonylurea (b) synthetic auxin and (c) a phenyl pyrazoline.

In another object of the present invention wherein the triazinyl sulfonyl urea is metsulfuron methyl, the synthetic auxin is fluroxypyr meptyl, the phenyl pyrazoline is pinoxaden.

In yet another object of the present invention is to provide a synergistic herbicidal composition comprising metsulfuron methyl, fluroxypyr meptyl and pinoxaden and other agrochemical additives in effective amounts.

In yet another object of the present invention is to provide a method for controlling undesired plants or inhibiting their growth, which comprises applying a herbicidally effective amount of the said composition to the undesired plants or to a place where they grow.

SUMMARY OF THE INVENTION

The present invention provides a novel synergistic herbicidal composition.

One aspect of the present invention is to provide a novel herbicidal composition comprising of (a) triazinyl sulfonylurea (b) synthetic auxin and (c) a phenyl pyrazoline.

Another aspect of the present invention the triazinyl sulfonyl urea is metsulfuron methyl, the synthetic auxin is fluroxypyr meptyl, and the phenyl pyrazoline is pinoxaden.

Another aspect of the present invention provides a synergistic herbicidal composition comprising of:

a) metsulfuron methyl in a range from 0.1% (w/w) to 2% (w/w),
b) fluroxypyr meptyl in a range from 5% (w/w) to 25% (w/w),
c) pinoxaden present in a range from 1% (w/w) to 10% (w/w), and
d) agrochemical additives.

Another aspect of the present invention provides a water dispersible granules (WDG) composition comprising of:

a) metsulfuron methyl in a range from 0.1% (w/w) to 2% (w/w),
b) fluroxypyr meptyl in a range from 5% (w/w) to 25% (w/w),
c) pinoxaden present in a range from 1% (w/w) to 10% (w/w), and
d) agrochemical additives.

In an aspect of the present invention, the suitable agrochemical additives are selected from a wetting agent, a dispersing agent, a defoamer, anti-caking agent, co-filler, and filler.

In an aspect of the present invention, the wetting agent is selected from the group comprising of sodium isopropyl naphthalene sulfonate, alkyl naphthalene sulfonate, Propol 990N, and sodium methyl cocoyl taurate, present in a range from 1% to 5%

(w/w).

In an aspect of the present invention, the dispersing agent is selected from the group comprising of sodium salt of naphthalene sulfonate condensate, condensed methyl naphthalene sulfonate, blend of anionic surfactant and Polycarboxylate (JEEMOL D18), sodium polycarboxylate, sodium lignosulfonate, Alkyl naphthalene sulfonate condensate and combination thereof, present in a range from 1% to 15% (w/w).

In an aspect of the present invention, the defoamer is silicon antifoam emulsion, present in a range from 0.1% to 1.5% (w/w).

In an aspect of the present invention, the anti-caking agent is silicon dioxide, present in an amount of 0.1% to 3% (w/w).

In an aspect of the present invention, the co-filler is ammonium sulphate, present in a range from 10% to 25% (w/w).

In an aspect of the present invention, the filler is china clay, present in Q.S.

Yet another aspect of the present invention provides a process for the preparation of a water dispersible granules (WDG) composition comprising of metsulfuron methyl, fluroxypyr meptyl and pinoxaden.

Yet another aspect of the present invention provides a synergistic composition comprising of metsulfuron methyl, fluroxypyr meptyl and pinoxaden formulation with an improved stability and ready to use herbicidal composition, having superior bio-efficacy compared to the individual formulations.

Yet another aspect of the present invention provides a method for controlling undesired plants or inhibiting their growth, which comprises applying a herbicidally

effective amount of the said composition to the undesired plants or to a place where they grow.

The present invention relates to herbicidal composition with synergistic activity. The composition contains three active ingredients that mutually complement each other when used together and exhibit activity that is greater than the activities of individual components when used alone.

The present invention discloses a three-way combination of metsulfuron methyl, fluroxypyr meptyl and pinoxaden, which results in synergistic mixture that is more effective than the individual compounds at the considered doses. The composition of the present invention decreases application rates of each of the active ingredients and is non-phytotoxic. Thus, it is effective to reduce the environmental load on an area where the composition is applied or a surrounding area thereof.

DESCRIPTION OF THE INVENTION

The term "comprising", which is synonymous with "including", "containing", or "characterized by" here is defined as being inclusive or open-ended, and does not exclude additional, unrecited elements or method steps, unless the context clearly requires otherwise.

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.

As used herein, the terms "crops" and "vegetation" can include, for instance, dormant seeds, germinant seeds, emerging seedlings, plants emerging from vegetative propagules, immature vegetation, and established vegetation.

As used herein, immature vegetation may be understood to include small vegetative plants prior to reproductive stage, and mature vegetation may be understood to include vegetative plants during and after the reproductive stage.

As used herein, the terms "herbicide" may be understood as a substance that is toxic to plants, used to destroy unwanted vegetation.

As used herein, the term "synergistic composition" may be understood to include effective combination of more than one agrochemical that allows the application of the said agrochemical in a much lower dosage, which results in a less dosage treatment for the crops.

As used herein, the term "agrochemical additives" may be understood to include a range of surfactants, dispersing agents, organic or inorganic pigments, solvents, de-solvents, defoamers, and emulsions, crystallization inhibitors, viscosity modifiers, suspending agents, dyes, antioxidants, foaming agents, light absorbers, mixing aids, neutralizers or pH adjusting substances and buffers, corrosion inhibitors, fragrances, wetting agents, absorption enhancers, micronutrients, plasticizers, lubricants, thickeners, anti-freezing agents, sterilization agents among others.

The herbicidal composition of the present invention may be formulated as 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 or

WDG), 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) among others. Preferably, the composition of the present invention is formulated as water dispersible granules (WDG).

One embodiment of the present invention is to provide a novel herbicidal composition comprising of (a) triazinyl sulfonylurea (b) synthetic auxin and (c) phenyl pyrazoline.

Another embodiment of the present invention, the triazinyl sulfonyl urea is metsulfuron methyl, the synthetic auxin is fluroxypyr meptyl, the phenyl pyrazoline is pinoxaden.

Another embodiment of the present invention provides a synergistic herbicidal composition comprising of:

a) metsulfuron methyl in a range from 0.1% (w/w) to 2% (w/w),
b) fluroxypyr meptyl in a range from 5% (w/w) to 25% (w/w),
c) pinoxaden present in a range from 1% (w/w) to 10% (w/w), and
d) agrochemical additives.

Another embodiment of the present invention provides a water dispersible granules (WDG) composition comprising of:

a) metsulfuron methyl in a range from 0.1% (w/w) to 2% (w/w),
b) fluroxypyr meptyl in a range from 5% (w/w) to 25% (w/w),
c) pinoxaden present in a range from 1% (w/w) to 10% (w/w), and
d) agrochemical additives.

According to the present invention, the suitable agrochemical additives are selected from a wetting agent, a dispersing agent, a defoamer, anti-caking agent, co-filler, and a filler.

According to the present invention, the wetting agent is selected from the group comprising of sodium isopropyl naphthalene sulfonate, alkyl naphthalene sulfonate, Propol 990N, and sodium methyl cocoyl taurate, present in a range from 1% to 5% (w/w).

According to the present invention, the dispersing agent is selected from the group comprising of sodium salt of naphthalene sulfonate condensate, condensed methyl naphthalene sulfonate, blend of anionic surfactant and Polycarboxylate (JEEMOL D18) , sodium polycarboxylate, sodium lignosulfonate, Alkyl naphthalene sulfonate condensate and combination thereof, present in a range from 1% to 15% (w/w).

According to the present invention, the defoamer is silicon antifoam emulsion, present in a range from 0.1% to 1.5% (w/w).

According to the present invention, the anti-caking agent is silicon dioxide, present in an amount of 0.1% to 3% (w/w).

According to the present invention, the co-filler is ammonium sulphate, present in a range from 10% to 25% (w/w).

According to the present invention, the filler is china clay, present in Q.S.

Yet another embodiment of the present invention provides a process for the preparation of a water dispersible granules (WDG) composition comprising of metsulfuron methyl, fluroxypyr meptyl and pinoxaden.

The composition of the present invention and method provided may be utilized to control weeds or battle undesired vegetation in crops or other settings, including but not limited to cereals, such as wheat, barley, rye, oats, corn/maize, rice, sorghum,

triticale and related crops; fruit, such as pomes, stone fruit and soft fruit, for example apples, grapes, pears, plums, peaches, almonds, cherries, and berries, for example strawberries, raspberries and blackberries; leguminous plants, for examples beans, lentils, peas, soybeans, peanut; oil plants, for example rape, mustard, and sunflower; cucurbitaceae, for example marrows, cucumbers, melons; fibre plants, for example cotton, flax, hemp, jute; citrus fruit, for example oranges, lemons, grapefruit and mandarins; vegetable, for example spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paparika; as well as ornamentals, such as flowers, shrubs, broad-leaved trees and evergreens, for example conifers, pastures, grasslands, rangelands, fallow and, turf, tree and vine orchards, and industrial vegetation management. Preferably, the undesirable vegetation includes species from the families of broadleaved and grass weeds, more preferably from the families of Aeschynomene, Ageratum, Amaranthus, Bidens, Brachiaria, Cenchrus, Cyperus, Digitaria, Echinochloa, Eclipta, Eleusine, Eragrostis Fimbristylis, Galinsoga, Ischaemum, Leptochloa, Monochoria, Panicum, Paspalum, Polygonum, Portulaca, Richardia, Sesbania, Setaria, Sida, Sorghum, most preferably Echinochloa, Leptochloa, Ischaemum, Monochoria, and Cyperus, or combinations thereof. It has been surprisingly found that the herbicidal composition of the present invention delays the appearance of the resistant strains of weeds and achieves effective and economical control of undesired weeds.

The composition achieves improved biological activity by enhancing overall control of weeds over a shorter period. Additional benefits of using the herbicidal composition of the present invention includes reduced risk of occupational hazard, lower cost of application, better cost: benefit ratio to the end user, reduced fuel, and labor cost, saving in applicator's time and loss caused by mechanical damage to the crop and soil.

The present compositions can be applied to the undesirable vegetation and/or weeds or their locus using conventional ground or aerial dusters, sprayers, and granule applicators, by addition to irrigation or paddy water, and by other conventional means known to those skilled in the art.

The present invention is further illustrated by the following examples which are provided merely to be exemplary of the inventions and is not intended to limit the scope of the invention. Certain modifications and equivalents will be apparent to those skilled in the art and are intended to be included within the scope of the present invention.

Examples:

Example-1: The illustrative embodiments show the composition of Metsulfuron methyl + fluroxypyr meptyl + Pinoxaden in water dispersible granules (WDG) form in different amount as follows:

Table-1: Metsulfuron methyl 0.5% + Fluroxypyr meptyl 15%+ Pinoxaden 5% WDG

S. No	Compositions	Function	Charge in (%)
1.	Metsulfuron methyl	Active ingredient	0.50
2.	Fluroxypyr meptyl	Active ingredient	15.0
3.	Pinoxaden	Active ingredient	5.0
4.	Alkyl naphthalene sulfonate	Wetting agent	5.0
5.	Sodium salt of naphthalene sulfonate condensate	Dispersing agent	2.0
6.	Silicone antifoam emulsion	Defoamer	0.5
7.	Silicon dioxide	Anti caking agent	1.0
8.	Ammonium sulphate	Co-filler	15.0
9.	China clay	Filler	Q.S.

Process for manufacture of composition is as follows:

Step 1: Weighing all the following raw materials according to the batch size in a pre-blender and mixing it for 1 hour.

- filler,
- co-filler,

- anticaking agent,
- wetting agent,
- dispersing agent,
- defoamer,
- metsulfuron methyl,
- fluroxypyr meptyl, and
- pinoxaden,

Step 2: Pre-mix the sample in a blender.

Step 3: Mill the sample, through Air Jet mill instrument.

Step 4: Collect the Air Jet milled sample and post blend in a blender.

Step 5: Prepare a mixture of water and defoamer for dough preparation.

Step 6: Extrude the granules through Basket extruder.

Step 7: Collect the WDG and dry in fluid bed dryer (FBD) @ 50°C, check the moisture content it should be < 5.0%.

Note: While drying the WDG in FBD, air flow rate should be maintained between 50-60.

Step 8: Submit the sample for Analysis.

Step 9: Pack the material appropriately (TLP bag).

Table-2: Metsulfuron methyl 0.2% + Fluroxypyr meptyl 10% + Pinoxaden 5% WDG

S. No	Compositions	Function	Charge in (%)
1.	Metsulfuron methyl	Active ingredient	0.2
2.	Fluroxypyr meptyl	Active ingredient	10.0
3.	Pinoxaden	Active ingredient	5.0
4.	Alkyl naphthalene sulfonate	Wetting agent	5.0
5.	Condensed methyl naphthalene sulfonate	Dispersing agent	10.0
6.	Ammonium sulphate	Co-filler	15.0
7.	Silicone antifoam emulsion	Defoamer	1.5

8.	Silicon dioxide	Anti caking agent	1.0
9.	China clay	Filler	Q.S.

The process for manufacture of composition is similar to the procedure as described in Table-1.

Table-3: Metsulfuron methyl 1.5% + Fluroxypyr meptyl 5% + Pinoxaden 10% WDG

S. No	Compositions	Function	Charge in (%)
1.	Metsulfuron methyl	Active ingredient	1.5
2.	Fluroxypyr meptyl	Active ingredient	5.0
3.	Pinoxaden	Active ingredient	10.0
4.	Sodium Polycarboxylate	Dispersing agent	5.0
5.	blend of anionic surfactant and Polycarboxylate (JEEMOL D18)	Dispersing agent	5.0
6.	Ammonium sulphate	Co-filler	15.0
7.	Silicone antifoam emulsion	Defoamer	0.1
8.	Silicon dioxide	Anti caking agent	1.0
9.	China clay	Filler	Q.S.

The process for manufacture of composition is similar to the procedure as described in Table-1.

Table-4: Metsulfuron methyl 0.1% + Fluroxypyr meptyl 20% + Pinoxaden 5% WDG

S. No	Compositions	Function	Charge in (%)
1.	Metsulfuron methyl	Active ingredient	0.1
2.	Fluroxypyr meptyl	Active ingredient	20.0
3.	Pinoxaden	Active ingredient	5.0

4.	Propol 990 N	Wetting agent	2.5
5.	Sodium lignosulfonate	Dispersing agent	10.0
6.	Ammonium sulphate	Co-filler	10.0
7.	Silicone antifoam emulsion	Defoamer	1.0
8.	Silicon dioxide	Anti caking agent	3.0
9.	China clay	Filler	Q.S.

The process for manufacture of composition is similar to the procedure as described in Table-1.

Table-5: Metsulfuron methyl 2% + Fluroxypyr meptyl 10% + Pinoxaden 5% WDG

S. No	Compositions	Function	Charge in (%)
1.	Metsulfuron methyl	Active ingredient	2.0
2.	Fluroxypyr meptyl	Active ingredient	10.0
3.	Pinoxaden	Active ingredient	5.0
4.	Sodium methyl cocoyl taurate	Wetting agent	5.0
5.	Alkyl naphthalene sulfonate condensate	Dispersing agent	12.0
6.	Ammonium sulphate	Co-filler	25.0
7.	Silicone antifoam emulsion	Defoamer	1.5
8.	Silicon dioxide	Anti caking agent	0.1
9.	China clay	Filler	Q.S.

The process for manufacture of composition is similar to the procedure as described in Table-1.

Example 2: Efficacy study of Metsulfuron methyl 0.5% + Fluroxypyr meptyl 15%+ Pinoxaden 5% in water dispersible granules (WDG) form:

SYNERGY STUDIES:

Wheat is the main cereal crop in India. In India, it is grown on an area of 31.6 million hectare with an annual production of 106.84 million tons. Successful weed control is the most important factor for fruitful wheat production because losses due to weeds have been one of the major limiting factors in wheat production. Weeds compete with crops for light moisture and nutrients. It was concluded that weeds exhibit economic yield losses to the wheat crop, which may range from 24-39.95% and these must be controlled during the full growing season of the crop for achieving satisfactory crop yields. Traditionally, weed control in India has been largely dependent on manual weeding. However, increased labour scarcity and costs are encouraging farmers to adopt herbicides.

Field studies were conducted to compare the weed controlling activity of the combination of Metsulfuron methyl, Fluroxypyr meptyl and Pinoxaden. **Metsulfuron Methyl** belongs to chemical class Sulfonylureas with ALS inhibitor (inhibition of acetolactate synthase) mode of action & **Fluroxypyr** meptyl belongs to Chemical class Pyridyloxy-carboxylates and its mode of action is based on AUXIN MIMICS. The active ingredient **Pinoxaden** in the combination, belongs to the chemical class of phenyl pyrazolines and its mode of action is based on inhibition of the Acetyl-coenzyme A carboxylase. Combination has the potential of controlling the cross-spectrum weeds (broad leaf weeds & grassy weeds) in wheat at the post-emergence (30-40 DAS or 10 days after 1st irrigation to wheat) application timing. All the molecules are safe to wheat when applied at their recommended dose rate in post-emergence (30-40 DAS or 10 days after 1st irrigation to wheat) application timing.

The weed control activity of the individual herbicides of the invention and their combinations were evaluated on weeds such as *Phalaris minor Malva parviflora, Melilotus alba & Rumex dentatus album*. Trials were conducted with randomized block

design with net plot size of 5 m x 6 m. Each trial was replicated four times and conducted under GEP guidelines. Spraying was done with manual operated backpack knapsack sprayer with 400 L of water spray volume per hectare at post-emergence application timing. Such field trials were carried out at various locations to generate independent data, the locations were chosen randomly across India.

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 the entire plot.

Appropriate analysis of plant response to herbicide combination is critical in determining the type of activity observed. The most widely used model is the 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

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

Table 6: Demonstrates synergy on weeds using the combination of Metsulfuron methyl, Fluroxypyr meptyl and Pinoxaden, in post-emergence application window. The field trials were carried out in India at various locations. The percentage efficacy was calculated after 30 days of application. The target weed was ***Phalaris minor,*** and the results are recorded in the table below.

Active	**Dose (GAH)**	**% Weed Control of *Phalaris minor***	
		Expected	**Observed**
Pinoxaden 5.1% EC	40		75
Metsulfuron methyl 20% WP	4		15
Fluroxypyr meptyl 20% EC	120		15
Pinoxaden 5.1% EC + Metsulfuron methyl 20% WP	40 + 4	78.75	75
Ratio of O/E		**0.95**	
Metsulfuron methyl 20% WP + Fluroxypyr meptyl 20% EC	4 + 120	27.75	20
Ratio of O/E		**0.72**	
Fluroxypyr meptyl 20% EC + Pinoxaden 5.1% EC	120 + 4	78.75	75
Ratio of O/E		**0.95**	
Metsulfuron methyl 0.5% + Fluroxypyr meptyl 15%+ Pinoxaden 5% WDG	164	81.93	85
Ratio of O/E		**1.03**	

EC – Emulsion concentrate; WP – Wettable powder; WDG – Water dispersible granules; and GAH – Gram Active per hectare.

The results in table 6, clearly demonstrate synergy between a three-way combination of Metsulfuron methyl, Fluroxypyr meptyl and Pinoxaden in post-emergence application timing against ***Phalaris minor.*** The higher ratio of the observed and the expected efficacy clearly demonstrates the synergistic effect of the combination. However, all two-way combinations showed lower ratio of the observed and the expected efficacy, which clearly showed the no synergistic effect of the combination against weeds like ***Phalaris minor.***

Table 7: Demonstrates synergy on weeds using the combination of Metsulfuron methyl, Fluroxypyr meptyl and Pinoxaden in post-emergence application window. The field trials were carried out in India at various locations. The percentage efficacy was calculated after 30 days of application. The target weed was ***Malva parviflora, Melilotus alba & Rumex dentatus*** and the results are recorded in the below tables.

Active	**Dose (GAH)**	**% Weed Control of *Malva parviflora***		**% Weed Control of *Melilotus alba***		**% Weed Control of *Rumex dentatus***	
		Expected	**Observed**	**Expected**	**Observed**	**Expected**	**Observed**
Pinoxaden 5.1% EC	40		10		5		5
Metsulfuron methyl 20% WP	4		40		85		70
Fluroxypyr meptyl 20% EC	120		80		82		85
Pinoxaden 5.1% EC + Metsulfuron methyl 20% WP	40 + 4	46	40	85.75	85	71.5	70
Ratio of O/E		**0.86**		**0.99**		**0.97**	
Metsulfuro	4 +	88	80	97.3	97	95.5	95

n methyl 20% WP + Fluroxypyr meptyl 20% EC	120						
Ratio of O/E		**0.98**		**0.99**		**0.99**	
Fluroxypyr meptyl 20% EC + Pinoxaden 5.1% EC	120 + 4	82	80	82.9	82	85.75	85
Ratio of O/E		**0.97**		**0.98**		**0.99**	
Metsulfuron methyl 0.5% + Fluroxypyr meptyl 15%+ Pinoxaden 5% WDG	164	89.2	95	97.4	100	95.72	100
Ratio of O/E		**1.01**		**1.02**		**1.04**	

EC – Emulsion concentrate; WP – Wettable powder; WDG – Water dispersible granules; and GAH – Gram Active per hectare.

The results in table 7, clearly demonstrate synergy between a three-way combination of Metsulfuron methyl, Fluroxypyr meptyl and Pinoxaden in post-emergence application timing against ***Malva parviflora, Melilotus alba & Rumex dentatus.*** The higher ratio of the observed and the expected efficacy clearly demonstrates the synergistic effect of the combination. However, all two-way combinations showed lower ratio of the observed and the expected efficacy, which clearly showed the no synergistic effect of the combination against weeds like, ***Malva parviflora, Melilotus alba & Rumex dentatus.***

WE CLAIM:

1. A synergistic herbicidal composition comprising of metsulfuron methyl, fluroxypyr meptyl, and pinoxaden.

2. The composition as claimed in claim 1, wherein the composition comprising of:
   a) metsulfuron methyl in a range from 0.1% (w/w) to 2% (w/w),
   b) fluroxypyr meptyl in a range from 5% (w/w) to 25% (w/w),
   c) pinoxaden present in a range from 1% (w/w) to 10% (w/w), and
   d) agrochemical additives.

3. The composition as claimed in claim 2, wherein the agrochemical additives are selected from a wetting agent, a dispersing agent, a defoamer, an anti-caking agent, a co-filler, and a filler.

4. The composition as claimed in claim 3, wherein the wetting agent is selected from sodium isopropyl naphthalene sulfonate, alkyl naphthalene sulfonate, Propol 990N, and sodium methyl cocoyl taurate, present in a range from 1% to 5% (w/w).

5. The composition as claimed in claim 3, wherein the dispersing agent is selected from sodium salt of naphthalene sulfonate condensate, condensed methyl naphthalene sulfonate, blend of anionic surfactant and Polycarboxylate (JEEMOL D18) , sodium polycarboxylate, sodium lignosulfonate, Alkyl naphthalene sulfonate condensate and combination thereof, present in a range from 1% to 15% (w/w).

6. The composition as claimed in claim 3, wherein the defoamer is silicone antifoam emulsion, present in a range from 0.1% to 1.5% (w/w).

7. The composition as claimed in claim 3, wherein the anti-caking agent is silicon dioxide, present in an amount of 0.1% to 3% (w/w).

8. The composition as claimed in claim 3, wherein the co-filler is ammonium sulphate, present in a range from 10% to 25% (w/w).

9. The composition as claimed in claim 3, wherein the filler is china clay, present in Q.S

10. The composition as claimed in claims 1 and 2, wherein the composition is formulated as water dispersible granules (WDG) form.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2023/061998

A. CLASSIFICATION OF SUBJECT MATTER
A01N47/36,A01N43/66,A01N43/40,A01N43/90 Version=2024.01

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

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	WO 2016/102504 A1 (MITSUI AGRISCIENCE INTERNATIONAL S.A/N.V. [IE]) 30 June, 2016 Table 1, pages 6-14, 22-24, claim 14	1-10
Y	WO 2017/140650 A1 (UPL EUROPE LTD [GB]) 24 August, 2017 page 9: lines 4-28; page 11: lines 28-31	1-10

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"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
18-03-2024	18-03-2024

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IB2023/061998

Citation	Pub.Date	Family	Pub.Date
WO 2016/102504 A1	30-06-2016	EP 3236750 A1	01-11-2017
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