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(54) Title: TERNARY HERBICIDAL COMPOSITION

(57) Abstract: The present invention relates to a novel synergistic herbicidal combination comprising Bispyribac sodium; Chlormuron ethyl; and Penoxsulam, which at particular concentration and dosage ranges provides enhanced effective control of sedges, narrow-leaved weeds and broad-leaved weeds in agricultural crops, particularly in Rice (*Oryza sativa*).



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TERNARY HERBICIDAL COMPOSITION

FIELD OF INVENTION

The present invention relates to a trimix herbicidal combination comprising Bispyribac sodium, Penoxsulam and Chlorimuron ethyl. In particular, the invention relates to a novel, synergistic and broad-spectrum herbicidal composition comprising said combination for the control of narrow leaved weeds, broad-leaved weeds and sedges in agricultural crops, particularly rice crop.

BACKGROUND OF THE INVENTION

Weed control is an important practice for crops growth. The losses caused by weeds in agricultural production environments include reduced crop quality, increased irrigation costs, increased harvesting costs, reduced land value, injury to livestock and crop damage from insects and pests harbored by the weeds. Further, weeds may compete with crop plants for the essential nutrients essential and may produce toxic or irritant chemicals that cause human or animal health problems. Some of the weed varieties also produce immense quantities of seed or vegetative reproductive parts or both that contaminate agricultural products and perpetuate the species in agricultural land.

Rice or *Oryza sativa* (Asian rice) is the most widely consumed staple food for a large part of the world's human population, especially in Asia. It has high nutritional value and provides instant energy and is an important part of the ideal complete diet. Besides this, rice straw is used as cattle feed and in preparation of various articles (hats, mats, ropes, etc.) in cottage industry. Rice husk is used as animal feed. Rice also has a significant medicinal value and is used for treating many health related maladies such as indigestion, diabetes, arthritis, paralysis, epilepsy and gives strength to pregnant and lactating mothers.

India is an important centre for rice cultivation. Rice is cultivated in a wide range of ecosystems, from irrigated to shallow lowlands, mid-deep lowlands and deep water to uplands. Weeds are however a major impediment to the production of rice and are responsible for heavy yield losses in rice fields, to the extent of complete crop loss under extreme conditions. In fact, out of the losses due to various biotic stresses, weeds are known to account for nearly one-third. Therefore, weed control is a major pre-requisite for improved productivity of rice in India, which is much required to meet the increasing nutritional demands of the growing population.

The present herbicidal combination is aimed at providing superior control of weeds with no crop injury and no carryover problems and additionally minimize the total amount of herbicide being

applied to cropland. The composition may be applied to a variety of agricultural crops, but has shown excellent effects in the control of weeds in rice crop.

Bispyribac sodium – chemically known as sodium 2,6-bis[(4,6-dimethoxypyrimidin-2-yl)oxy]benzoate [CAS registration no. 125401-92-5] is a broad spectrum post emergent herbicide that effectively controls grasses, sedges and broad leaf weeds infesting rice crop both in nursery and main field. After application, it gets absorbed by foliage and roots. It has excellent rice crop selectivity and it degrades in plant system extremely fast to provide an excellent control of all major weeds with utmost safety to rice crop when applied as post emergent herbicide. It has wide application window and can be used in early post emergent segment.

Penoxsulam chemically known as 2-(2,2-difluoroethoxy)-N-(5,8- dimethoxy-[1,2,4] triazolo[1,5-c]pyrimidin-2-yl)-6(trifluoromethyl)benzenesulfonamide is effective in control of *Echinochloa* spp., as well as many broad-leaved, sedge and aquatic weeds such as *Alisma plantago-aquatica*, *Ammania coccinea*, *Cyperus difformis* and *Scirpus mucronatus*) in rice crop. Penoxsulam is a branched chain amino acid (leucine, isoleucine and valine) synthesis (ALS –Acetolactate synthase) inhibitor. The selective action is based on differential metabolism to inactive metabolites. Penoxsulam has a systemic action, and is absorbed mainly via leaves, and secondarily via roots, and is translocated in both phloem and xylem. Penoxsulam is mainly applied as post-emergence herbicide that causes immediate growth inhibition, and plants become reddish at the tips.

Chlorimuron ethyl is a sulfonylurea class herbicide which is a branched chain amino acid synthesis (ASL or AHAS) inhibitor. It acts by inhibiting biosynthesis of the essential amino acids valine and isoleucine, hence stopping cell division and plant growth. Crop selectivity derives from plant metabolism both by homo glutathione conjugation and by de-esterification. It is a highly effective post emergence herbicide for control of economically important broadleaf weeds in soybean. It is a potent inhibitor of plant cell division and growth. Inhibition of growth is rapid in the growing tips of both the roots and shoots of the sensitive plants.

Although the above active ingredients are individually known for their herbicidal actions, there is a need in the art for a single ready to use composition that offers multiple advantages like enhanced control of weeds, reduced Active Ingredient (AI) dosage thereby resulting into reduced soil residues, broader spectrum of control of weeds-narrow leaved weeds, broad leaved weeds and sedges, broader application window (early post emergence 9-14 days after transplanting; post emergence 18-24 days after transplanting), environmentally safe formulation with low applicator hazard and little dust and non-phytotoxicity to target crops.

It must however be appreciated that the process of combining the individual AIs or formulating one or more herbicides in a single composition poses many challenges to the formulator. Major challenges being physical, chemical and biological incompatibility, a lack of stability in a co-
5 formulation, decomposition of an active compound, or antagonism of the active compounds. Therefore, a stable single use formulation is not guaranteed and requires rigorous experimentations and trials. Some combination formulations are also known in the prior art, however these do not offer the multiple advantages as offered by the presently claimed herbicidal composition.

10 CN106165686 provides a herbicide for dry-field crops. Active components comprise Pendimethalin, Bispyribac sodium and Quizalofop-ethyl. The mass ratio of Pendimethalin, Bispyribac sodium and Quizalofop-p-ethyl is 5-30:1-20:1-20. The herbicide composition comprises 7-70% by weight of the active components, with the balance being auxiliary agent.
15 Said invention provides a herbicidal mixture for dry-field crops, which is efficient, low in toxicity, environmental friendly and capable of facilitating comprehensive field weed control.

CN103621508 discloses a stem and leaf herbicide for a paddy field and a preparation method thereof, and in particular relates to a Bispyribac-sodium dispersible oil suspended agent and a
20 preparation method thereof. Said Bispyribac-sodium dispersible oil suspended agent comprises the following components in percentage by mass: 10-20 percent of Bispyribac-sodium, 2-30 percent of emulsifier, 0.2-5 percent of a wetting agent, 0.3-5 percent of a dispersing agent, 0.5-4 percent of a thickening agent, 0.01-5 percent of a defoaming agent, 0.1-1.5 percent of a pH regulating agent, and the balance of an oil-based solvent.

25 Thus, there remains a need to develop a herbicidal combination and composition that helps to achieve the weedcidal action at lower application rates accompanied with other advantages as described later in the specification.

30 OBJECT OF THE INVENTION

It is an object of the present invention to provide a novel, synergistic, broad spectrum herbicidal combination of Bispyribac sodium, Chlorimuron ethyl and Penoxsulam for effective control of

broad-leaved weeds, narrow leaved weeds and sedges in agricultural crops, particularly Rice crop.

SUMMARY OF THE INVENTION

5 In an aspect, the present invention provides a herbicidal combination comprising a) a herbicidally effective amount of Bispyribac sodium b) a herbicidally effective amount of Penoxsulam and c) a herbicidally effective amount of Chlorimuron ethyl.

10 In another aspect, the present invention provides a herbicidal composition comprising a) a herbicidally effective amount of Bispyribac sodium b) a herbicidally effective amount of Penoxsulam and c) a herbicidally effective amount of Chlorimuron ethyl along with at least one agriculturally acceptable excipient.

15 In yet another aspect, the present invention provides a method for controlling undesired weeds in rice crop, said method comprising treating the locus at which rice crop is growing or intended to be grown with a herbicidal combination comprising a) a herbicidally effective amount of Penoxsulam and c) a herbicidally effective amount of Chlorimuron ethyl along with at least one agriculturally acceptable excipient.

20 In yet another aspect, the present invention provides a process of preparing the herbicidal composition of the present invention, said process comprising the specified steps.

25 In yet another aspect, the present invention provides a herbicidal composition that has a broader application window (early post emergence 9-14 days after transplanting; post emergence 18-24 days after transplanting),

DETAILED DESCRIPTION OF THE PRESENT INVENTION

Those skilled in the art will be aware that the invention described herein is subject to variations and modifications other than those specifically described. It is to be understood that the invention described herein includes all such variations and modifications. The invention also includes all such steps, features, compositions, and compounds referred to or indicated in this specification, individually or collectively, and all combinations of any two or more of said steps

30

or features.

Unless otherwise specified, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of the ordinary skill in the art to which the invention belongs. For further guidance, term definitions may be included to better appreciate the teaching of the present invention.

As used herein, the term “plant” refers to any plant or part thereof including aerial and subterranean parts of the plant. It is contemplated that the parts of the plant may be, for example, flowers, fruits or vegetables, shoots, leaves, needles, stalks, stems, fruiting bodies, seeds, also roots and that parts of the plants may or may not be attached to the remainder of the plant.

As used herein, the term “weed” refers to the unwanted plant which competes for resources with the crop or plant of interest.

As used herein, the term “herbicide” refers to a substance which adversely affects the existence and growth of the target weed.

As used herein the term “effective amount” is that quantity of active agent, applied in an amount which will provide the required control of weed on commercial crops. The amount is dependent upon many factors including, for example, type of formulations, the crop, weed sought to be controlled and environmental conditions.

As used herein, the term “agriculturally acceptable excipient” refers to an ingredient, additive, component or supplement, liquid or solid, suitable for incorporation in agricultural compositions.

As used herein, the terms “comprise”, “comprises”, “comprising”, “include”, “includes”, and “including” are meant to be non-limiting ie. other steps and other ingredients which do not affect the end of result can be added. The above terms encompass the terms “consisting of” and “consisting essentially of”.

The terms “weight percent”, “wt-%”, “percent by weight”, “% by weight” and variations thereof, as used herein, refer to the concentration of a substance as the weight of that substance divided by the total weight of the composition and multiplied by 100. It is understood that, as used here, “percent”, “%” and the like are intended to be synonymous with “weight percent”, “wt. %”, etc. The present invention provides a herbicidal composition comprising a) Bispyribac Sodium b) Chlorimuron ethyl and c) Penoxsulam wherein Bispyribac Sodium is present in an amount ranging from 18 to 40% w/w, Chlorimuron ethyl is present in an amount ranging from 3 to 6% w/w and Penoxsulam is present in an amount ranging from 6 to 25 % w/w of the herbicidal composition.

In a preferred embodiment, Bispyribac sodium is present in an amount 24% w/w, Chlorimuron ethyl is present in an amount of 4.8% w/w and Penoxsulam is present in an amount of 12% w/w and of the herbicidal composition.

In an embodiment, the herbicidal composition of the present invention comprising the said
5 actives exhibits synergistic effect and provides a broad spectrum control of narrow leaved weeds, broad leaved weeds and sedges in agricultural crops, particularly in Rice.

In an embodiment, the herbicidal composition of the present invention has a broader application window (early post emergence 9-14 days after transplanting; post emergence 18-24 days after transplanting).

10 Surprisingly, the present inventors have now found that the presently claimed herbicidal composition when applied at significantly lesser dosages than recommended dosages when applied separately, exhibited superior efficacy as measured in terms of percent control of target weeds. In other words, it was surprising to find that these conventional rice herbicides when combined at desired wt. percentages at reduced individual AI dosages, the resulting efficacy in
15 controlling undesirable weeds in paddy is unexpectedly enhanced.

Further surprisingly, it has been found that the active compound combination of the presently claimed composition exhibits a synergistic effect and not merely an additive effect. Thus, clearly, the customary dosages of the individual actives is substantially reduced, leading to lesser amount of soil residues and environmental pollution when the composition of the present invention is
20 used.

In an embodiment, the herbicidal composition further comprises at least one agriculturally acceptable excipient. In an embodiment, the at least one excipient is selected from the group consisting of at least a wetting agent, at least a dispersing agent, at least a defoaming agent, at least a binder, at least a suitable carrier, and combinations thereof. In a preferred embodiment,
25 the herbicidal composition is in the form of a wettable granule formulation further comprising at least a wetting agent, at least a dispersing agent, at least a defoaming agent, at least a binder, and at least a suitable carrier.

In an embodiment, the at least a dispersing agent is selected from the group consisting of sodium lignosulphonates, sodium naphthalene sulphonate- formaldehyde condensates, aliphatic alcohol ethoxylates, tristyrylphenol ethoxylates and esters, ethylene oxide/propylene oxide block
30 copolymers, and combinations thereof. In a preferred embodiment, the at least a dispersing agent is sodium salt of naphthalene sulfonate condensate. The at least a dispersing agent weight

concentration in said herbicidal composition is in the range of 5 to 20 %w/w. In a preferred embodiment, the dispersing agent is present in an amount of 10% w/w.

In an embodiment, the at least a wetting agent is selected from the group consisting of blend of alkyl naphthalene sulfonate, sodium salt, sodium laurel sulphate, and combinations thereof. In a preferred embodiment, the at least a wetting agent is sodium laurel sulphate. The at least a wetting agent weight concentration in said herbicidal composition is in the range of 2 to 8% w/w. In a preferred embodiment, the wetting agent is present in an amount of 4% w/w.

In an embodiment, the at least an anti-foaming is selected from the group consisting of silicone emulsions, long-chain alcohols, fatty acids, organic fluorine compounds, and combinations thereof. The at least an anti-foaming agent weight concentration in said herbicidal composition is in the range of 0.2 to 1% w/w. In a preferred embodiment, the antifoaming agent is present in an amount of 0.5% w/w.

In an embodiment, the at least a binder is selected from the group consisting of Starch paste, Hydroxypropyl methyl cellulose (HPMC), Polyvinyl Pyrrolidone (PVP), Lactose monohydrate, and combinations thereof. The at least a binder weight concentration in said herbicidal composition is in the range of 5 -10% w/w. In a preferred embodiment, the binder is present in an amount of 8% w/w.

In an embodiment, the at least a carrier is selected from the group consisting of dextrose, lactose, soluble starch, galactose, amyloextrin, ammonium sulfate, maltose, mannitol, sucrose, sorbitol, china clay, and combinations thereof. In a preferred embodiment, the carrier is china clay. In an embodiment, the carrier is added in a balance amount (post addition of all other adjuvants) of the composition.

In an embodiment, the herbicidal composition is formulated in a form selected from the group consisting of water-soluble concentrates (SL), emulsifiable concentrates (EC), emulsions (EW), micro-emulsions (ME), Suspension concentrates (SC), oil-based suspension concentrates (OD), flowable suspensions (FS), water-dispersible granules (WG), water-soluble granules (SG), wettable powders (WP), water soluble powders (SP), granules (GR), encapsulated granules (CG), fine granules (FG), macrogranules (GG), dry flowables (DF), aqueous Suspo-emulsions (SE), capsule suspensions (CS) and microgranules (MG). In a preferred embodiment, the herbicidal composition is in the form of suspension concentrates (SC), water-dispersible granule (WDG) and wettable powder (WP).

In a more preferred embodiment, the herbicidal composition of the present invention is

formulated in the form of water dispersible granule (WDG) comprising a wetting agent, a dispersing agent, a defoaming agent, a binder and a suitable carrier.

The present invention also provides a method for controlling undesired weeds in agricultural crops, particularly in rice crop, said method comprising treating rice crop with a herbicidal composition comprising a) Bispyribac sodium b) Chlorimuron ethyl and c) Penoxsulam, wherein Bispyribac sodium is present in an amount ranging from 18 to 40 % w/w, Chlorimuron ethyl is present in an amount ranging from 3 to 6% w/w and Penoxsulam is present in an amount ranging from 6 to 25 % w/w of the herbicidal composition.

In a preferred embodiment, Bispyribac sodium is present in an amount of 24% w/w, Chlorimuron ethyl is present in an amount of 4.8 % w/w and Penoxsulam is present in an amount of 12% w/w of the herbicidal composition. The herbicidal composition is as described substantially in the present disclosure.

In an embodiment, the herbicidal composition is applied at a dosage in the range of 120-160 gm/ha. In a preferred embodiment, the herbicidal composition of the present invention is applied at a dosage of 125gms/ha.

The present invention further provides a process of preparing a herbicidal composition comprising a) Bispyribac sodium b) Chlorimuron ethyl and c) Penoxsulam, wherein Bispyribac sodium is present in an amount ranging from 18 to 40% w/w, Chlorimuron ethyl is present in an amount ranging from 3 to 6% w/w and Penoxsulam is present in an amount ranging from 6 to 25% w/w of the herbicidal composition; as a water-dispersible formulation, said process comprising the following steps:

1. The desired quantity of active ingredients and excipients were weighed and mixed in a blender.
2. The mixture was subjected to grinding through a jet mill and grinding was carried out until a mean particle size of below 10 micron was obtained.
3. The homogenous mix was again put in a blender and a dough was prepared by dough mixer.
4. The granules were prepared by carrying the dough through an extruder.
5. The granules thus prepared were dried by using hot air or and oven.
6. The dried granules were checked for quality parameters (described in example 1 below)

EXAMPLES

The examples below are given solely for the purpose of illustration and are not to be construed

as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

Example 1: Preparation of herbicidal composition as wettable granule (WG)

Table 1 below provides a herbicidal composition as described in the present specification, formulated as a wettable granule (WG)

Table 1: Composition of the herbicidal composition (CH24124WG)

Ingredient	Tentative percentage w/w
Bispyribac technical (Basis of 100.0%)	24.00%
Penoxsulam technical (Basis of 100.0%)	12.00%
Chlorimuron technical (Basis of 100%)	4.80%
Ammonium sulphate	5.00%
Lactose	8.00%
Sodium salt of naphthalene sulfonate condensate (Dispersing agent)	10.00%
Sodium laurel sulphate (Wetting agent)	4.00%
Antifoam	0.50%
China clay	QS to make %

Preparation method of WG

The desired quantity of the active ingredients and excipients were weighed and mixed in a blender. The mixture was then subjected to grinding through a jet mill and grinding was carried out until a mean particle size of below 10 micron was obtained. After grinding, the homogenous mix was again put in a blender and a dough was prepared by dough mixer. After this step, granules were prepared by carrying the dough through an extruder. The granules thus prepared were then dried by using hot air or and oven. The dried granules were then checked for quality parameters.

The WG formulation as described above in Table 1 was tested for the below mentioned quality parameters as listed in Table 2.

Table 2: Quality parameters of WG formulation

S.no.	Parameter	Desired quality
1.	Description	Description – the material shall consist of dry, free

S.no.	Parameter	Desired quality
		flowing granules, shall wet on mixing with water providing solution suitable for spray. The material shall be free from visible extraneous matter.
2.	A.I. Content	Bispyribac -24% m/m ($\pm 5\%$) Penoxsulam -12% m/m ($\pm 5\%$) Chlorimuron -4.8% m/m ($\pm 10\%$)
3.	Persistent foaming	not more than 60 ml after 1 min
4.	Wettability	max 120 sec.
5.	Suspensibility	Suspensibility- 60% min.
6.	Acidity	Acidity as H ₂ SO ₄ – 0.5% max

Example 2: Field evaluation of the bioefficacy of the present herbicidal composition

Location/season/crop: The presently disclosed herbicidal trimix (coded as CH24124WG) was tested for its bioefficacy against narrow leaved weeds, broad leaved weeds and sedges in rice crop. The trial was conducted during Kharif season 2020 at Rudrapur, Uttarakhand on Pusa -44 variety of rice.

Trial layout: The plants were aligned in a plot size of 450 sq. meter, with the spacing of 10 cm between individual crop plants and the same spacing of 10 cm between the rows. The trial was laid out in a random block design consisting of a total of 16 treatments in three replications.

Climatic conditions: The trial was conducted at a temp. 35°C under 85% relative humidity with no winds.

Application: The application of the herbicidal trimix was carried out at post emergence stage 22 days after transplanting and at 2-4 leaves stage of weed. 2-3 cms of standing water was maintained in the main field after application.

Measured quantity of the chemical was added to required volume of water @ 375 lit. /ha for spray. The spray tank was filled with ½ the quantity of clean required volume of water and then the measured chemical (according to the dose) was added followed by the rest half quantity of water. The solution was stirred well before application. Knapsack sprayer fitted with boom along with flood jet nozzle was used to apply the herbicidal composition.

Table 3 below provides the treatment details. (For purposes of convenience, the present

composition has been represented by the code CH24124WG)

Table 3

Trial no.	Treatment details	Dose a.i (g)./ha	Dose in g/ha
T-1	Untreated	-	-
T-2	Bispyribac sodium 10 SC	37.5	375
T-3	Penoxsulam 2.67 OD	25	1000
T-4	Chlorimuron ethyl 25 WP	6	24
T-5	CH-24124 WG	27 + 13.5 + 5.4	112.5
T-6	CH-24124 WG	30 + 15 + 6.0	125
T-7	CH-24124 WG	33 + 16.5 + 6.6	137.5
T-8	CH-20835 WG	25 + 10 + 4.38	125
T-9	CH-20835 WG	30 + 12 + 5.25	150
T-10	CH-20835 WG	35 + 14 + 6.13	175
T-11	CH-30154 WG	30 + 15 + 4	100
T-12	CH-30154 WG	33 + 16.5 + 4.4	110
T-13	CH-30154 WG	36 + 18 + 4.8	120
T-14	CH-35105 WG	28 + 8 + 4	80
T-15	CH-35105 WG	31.5 + 9 + 4.5	90
T-16	CH-35105 WG	35 + 10 + 5	100

Note

CH-24124 WG (Bispyribac sodium 24% + Penoxsulam 12% + Chlorimuron ethyl 4.8% WG

CH-20835 WG (Bispyribac sodium 20% + Penoxsulam 8% + Chlorimuron ethyl 3.5% WG

CH-30154 WG (Bispyribac sodium 30% + Penoxsulam 15% + Chlorimuron ethyl 4.0% WG

CH-35105 WG (Bispyribac sodium 35% + Penoxsulam 10% + Chlorimuron ethyl 5.0% WG

Example 3: Evaluation of bio-efficacy in paddy

The weed control efficacy was calculated as percent weed control as follows:

Weed count: A quadrat (0.5m × 0.5m) was placed at 3 randomly selected places in all the plots of the experimental field and the number of weed flora were counted uniformly at 14 and 28 days after application

Weed control: The weed control was calculated based on no. of live weed flora at 14 and 28 days after application.

Percent weed control = $WC - WT$

..... $\times 100$

WC

Where WC= No. of weed in control plot

WT= No. of weed in treated plot

5

Table 4: Effect of herbicidal treatment on weed density of narrow and broad-leaved weeds at 14DAA

Treatments	Dose (a.i/ha)	Percent control of Narrow leaves & Broad weeds (Mean 0.25 sqm) over UTC					
		<i>Echinochloa spp.</i>		<i>Marselia spp.</i>		<i>Cyperus iria</i>	
		Live pop.	% Control	Live pop.	% Control	Live pop.	% Control
Untreated	-	25	-	14	-	10	-
Bispyribac sodium 10 SC	37.5	7.0	72.0	5.0	64.28	4.0	60.0
Penoxsulam 2.67 OD	25	9.0	64.0	6.0	57.14	2.0	80.0
Chlorimuron ethyl 25 WP	6	17.0	32.0	8.0	42.85	2.0	80.0
CH-24124 WG (EX-1)	27 + 13.5 + 5.4	3.0	88.0	2.0	85.71	1.0	90.0
CH-24124 WG	30 + 15 + 6.0	2.0	92.0	0.0	100.0	0.5	95.0
CH-24124 WG	33 + 16.5 + 6.6	1.0	96.0	0.0	100.0	0.5	95.0
CH-20835 WG (EX-2)	25 + 10 + 4.38	3.0	88.0	2.0	85.71	3.0	70.0
CH-20835 WG	30 + 12 + 5.25	2.5	90.0	1.5	89.28	2.5	75.0
CH-20835 WG	35 + 14 + 6.13	2.0	92.0	1.5	89.28	2.0	80.0
CH-30154 WG (EX-3)	30 + 15 +	3.0	88.0	2.0	85.71	4.0	60.0

	4						
CH-30154 WG	33 + 16.5 + 4.4	3.0	88.0	0.0	100.0	3.0	70.0
CH-30154 WG	36 + 18 + 4.8	2.0	92.0	0.0	100.0	2.5	75.0
CH-35105 WG (EX-4)	28 + 8 + 4	4.0	84.0	3.0	78.57	3.0	70.0
CH-35105 WG	31.5 + 9 + 4.5	3.0	88.0	2.0	85.71	2.0	80.0
CH-35105 WG	35 + 10 + 5	2.5	90.0	2.0	85.71	2.0	80.0

EX-1, 2, 3, 4 represent the AI percent variants tested

As seen in Table 4, Bispyribac sodium treatment alone at the practiced dosage of 37.5g a.i./ha results in 72% control of *Echinochloa* spp., about 64% control of *Marselia* spp., and 60% control of *Cyperus iria*. Penoxsulam treatment alone at the practiced dosage of 25g a.i./ha results in 64% control of *Echinochloa* spp., about 57% control of *Marselia* spp., and 80% control of *Cyperus iria*. Chlorimuron ethyl treatment alone at the practiced dosage of 6g a.i./ha results in 32% control of *Echinochloa* spp., about 42% control of *Marselia* spp., and 80% control of *Cyperus iria*.

Unexpectedly and surprisingly, it was found that the composition coded CH-24124 WG (EX-1) comprising Bispyribac sodium at 27g a.i./ha + Penoxsulam at 13.5g a.i./ha + Chlorimuron ethyl at 5.4g a.i./ha results in 88% control of *Echinochloa* spp., about 85% control of *Marselia* spp. and 90% control of *Cyperus iria*. The composition coded CH-20835 WG (EX-2) comprising Bispyribac sodium at 25g a.i./ha + Penoxsulam at 10g a.i./ha + Chlorimuron ethyl at 4.38g a.i./ha results in 88% control of *Echinochloa* spp., about 85% control of *Marselia* spp., and 70% control of *Cyperus iria*. The composition coded CH-30154 WG (EX-3) comprising Bispyribac sodium at 30g a.i./ha + Penoxsulam at 15g a.i./ha + Chlorimuron ethyl at 4g a.i./ha results in 88% control of *Echinochloa* spp., about 85% control of *Marselia* spp., and 60% control of *Cyperus iria*. The composition coded CH-35105 WG (EX-4) comprising Bispyribac sodium at 28g a.i./ha + Penoxsulam at 8g a.i./ha + Chlorimuron ethyl at 4g a.i./ha results in 84% control of *Echinochloa* spp., about 78% control of *Marselia* spp., and 70% control of *Cyperus iria*.

These data clearly establish that the combination of the present invention has superior efficacy at lower effective concentrations compared to the effect at higher concentrations of the individual Active ingredient actually used in farmer practice.

Table 5-: Effect of herbicidal treatment on weed density of Narrow& Broad-leaved weeds at 28 DAA

Treatments	Dose (a.i/ha)	Percent control of Narrow leaves & Broad weeds (Mean 0.25 sqm) over UTC					
		<i>Echinochloa spp.</i>		<i>Marselia spp.</i>		<i>Cyperus iria</i>	
		Live pop.	% Control	Live pop.	% Control	Live pop.	% Control
Untreated	-	30	-	17	-	14	-
Bispyribac sodium 10 SC	37.5	9.0	70.0	7.0	58.8	5.0	64.3
Penoxsulam 2.67 OD	25	11.0	63.3	8.0	52.9	3.0	78.6
Chlorimuron ethyl 25 WP	6	19.0	36.6	10.0	41.1	3.0	78.6
CH-24124 WG (EX-1)	27 + 13.5 + 5.4	6.0	80.0	4.0	76.4	2.0	85.7
CH-24124 WG	30 + 15 + 6.0	4.0	86.6	2.0	88.2	1.5	89.3
CH-24124 WG	33 + 16.5 + 6.6	2.0	93.3	2.0	88.2	1.5	89.3
CH-20835 WG (EX-2)	25 + 10 + 4.38	7.0	76.6	4.0	76.5	4.0	71.4
CH-20835 WG	30 + 12 + 5.25	6.5	78.3	3.5	79.4	3.5	75.0
CH-20835 WG	35 + 14 + 6.13	5.0	83.3	3.5	79.4	3.0	78.6
CH-30154 WG (EX-3)	30 + 15 + 4	7.0	76.6	4.0	76.4	5.0	64.3
CH-30154 WG	33 + 16.5 + 4.4	6.0	80.0	2.0	88.2	4.0	71.4
CH-30154 WG	36 + 18 + 4.8	5.0	83.3	2.0	88.2	3.5	75.0
CH-35105 WG (EX-4)	28 + 8 + 4	6.0	80.0	5.0	70.6	4.0	71.4
CH-35105 WG	31.5 + 9 + 4.5	5.0	83.3	4.0	76.5	3.0	78.6

Treatments	Dose (a.i./ha)	Percent control of Narrow leaves & Broad weeds (Mean 0.25 sqm) over UTC					
		<i>Echinochloa spp.</i>		<i>Marselia spp.</i>		<i>Cyperus iria</i>	
		Live pop.	% Control	Live pop.	% Control	Live pop.	% Control
CH-35105 WG	35 + 10 + 5	4.5	85.0	4.0	76.5	3.0	78.6

EX-1, 2, 3, 4 represent the AI percent variants tested

As seen in Table 5, Bispyribac sodium treatment alone at dosage of 37.5g a.i./ha results in 70% control of *Echinochloa* spp., about 59% control of *Marselia* spp., and 64% control of *Cyperus iria*. Penoxsulam treatment alone at dosage of 25g a.i./ha results in 63% control of *Echinochloa* spp., about 53% control of *Marselia* spp., and 78% control of *Cyperus iria*. Chlorimuron ethyl treatment alone at dosage of 6g a.i./ha results in 36% control of *Echinochloa* spp., about 41% control of *Marselia* spp., and 78% control of *Cyperus iria*.

Unexpectedly and surprisingly, it was found that the composition coded as CH-24124 WG (EX-1) comprising Bispyribac sodium at 27g a.i./ha + Penoxsulam at 13.5g a.i./ha + chlorimuron ethyl at 5.4g a.i./ha results in 80% control of *Echinochloa* spp., about 76% control of *Marselia* spp., and 86% control of *Cyperus iria*. The composition coded CH-20835 WG (EX-2) comprising Bispyribac sodium at 25g a.i./ha + Penoxsulam at 10g a.i./ha + Chlorimuron ethyl at 4.38g a.i./ha results in 77% control of *Echinochloa* spp., about 77% control of *Marselia* spp., and 71% control of *Cyperus iria*. The composition coded CH-30154 WG (EX-3) comprising Bispyribac sodium at 30g a.i./ha + Penoxsulam at 15g a.i./ha + Chlorimuron ethyl at 4g a.i./ha results in 77% control of *Echinochloa* spp., about 76% control of *Marselia* spp., and 64% control of *Cyperus iria*. The composition coded CH-35105 WG (EX-4) comprising Bispyribac sodium at 28g a.i./ha + Penoxsulam at 8g a.i./ha + Chlorimuron ethyl at 4g a.i./ha results in 80% control of *Echinochloa* spp., about 71% control of *Marselia* spp., and 71% control of *Cyperus iria*.

These data clearly establish that the combination of the present invention has superior efficacy at lower effective concentrations compared to the effect at higher concentrations used in farmer practice.

Example 4: Evaluation of Phytotoxicity

A) Visual observations

Visual observations were recorded at 3, 7 and 10 days after application (DAA) of testing products. The parameters were observed leaf injury on tip/surface, necrosis, vein clearing, epinasty, hyponasty and wilting. The score scale (1-10) followed for leaf injury on tips/surface is given.

Table 6: Phytotoxicity symptoms scoring and rating for leaf injury on tip/surface

(B)	Leaf injury on tips/surface	Rating
	0-10%	1
	11-20%	2
	21-30%	3
	31-40%	4
	41-50%	5
	51-60%	6
	61-70%	7
	71-80%	8
	81-90%	9
	91-100%	10

Phytotoxicity studies

Table 7. Phytotoxic effect of various treatments on Rice crop after 3 DAA

Trial no.	Treatment details	Dose a.i./ha	3 DAA					
			L	N	V	E	H	W
T-1	Untreated	-	-	-	-	-	-	-
T-2	Bispyribac sodium 10 SC	37.5	0	0	0	0	0	0
T-3	Penoxsulam 2.67 OD	25	0	0	0	0	0	0
T-4	Chlorimuron ethyl 25 WP	6	0	0	0	0	0	0
T-5	CH-24124 WG (EX-1)	27 + 13.5 + 5.4	0	0	0	0	0	0
T-6	CH-24124 WG	30 + 15 + 6.0	0	0	0	0	0	0
T-7	CH-24124 WG	33 + 16.5 + 6.6	0	0	0	0	0	0
T-8	CH-20835 WG (EX-2)	25 + 10 + 4.38	0	0	0	0	0	0

T-10	CH-20835 WG	30 + 12 + 5.25	0	0	0	0	0	0
T-11	CH-20835 WG	35 + 14 + 6.13	1	3	0	1	0	0
T-12	CH-30154 WG (EX-3)	30 + 15 + 4	0	0	0	0	0	0
T-13	CH-30154 WG	33 + 16.5 + 4.4	0	0	0	0	0	0
T-14	CH-30154 WG	36 + 18 + 4.8	1	3	0	1	0	0
T-15	CH-35105 WG (EX-4)	28 + 8 + 4	0	0	0	0	0	0
T-16	CH-35105 WG	31.5 + 9 + 4.5	0	0	0	0	0	0
T-17	CH-35105 WG	35 + 10 + 5	1	3	0	1	0	0

DAA – Days after application,

L- Leaf injury on tips/surface, N-Necrosis, V- Vein clearing, E- Epinasty, H- Hyponasty, W-wilting

As seen in Table 7, it can be appreciated that the composition of the present invention is not phytotoxic to various plant parts even though they are more effective against various weeds.

Table-8. Phytotoxic effect of various treatments on wheat crop after 7 DAA

Trial no.	Treatment details	Dose a.i./ha	7 DAA					
			L	N	V	E	H	W
T-1	Untreated	-	-	-	-	-	-	-
T-2	Bispyribac sodium 10 SC	37.5	0	0	0	0	0	0
T-3	Penoxsulam 2.67 OD	25	0	0	0	0	0	0
T-4	Chlorimuron ethyl 25 WP	6	0	0	0	0	0	0
T-5	CH-24124 WG (EX-1)	27 + 13.5 + 5.4	0	0	0	0	0	0
T-6	CH-24124 WG	30 + 15 + 6.0	0	0	0	0	0	0
T-7	CH-24124 WG	33 + 16.5 + 6.6	0	0	0	0	0	0
T-8	CH-20835 WG (EX-2)	25 + 10 + 4.38	0	0	0	0	0	0
T-10	CH-20835 WG	30 + 12 + 5.25	0	0	0	0	0	0

T-11	CH-20835 WG	35 + 14 + 6.13	1	3	0	1	0	0
T-12	CH-30154 WG (EX-3)	30 + 15 + 4	0	0	0	0	0	0
T-13	CH-30154 WG	33 + 16.5 + 4.4	0	0	0	0	0	0
T-14	CH-30154 WG	36 + 18 + 4.8	1	3	0	1	0	0
T-15	CH-35105 WG (EX-4)	28 + 8 + 4	0	0	0	0	0	0
T-16	CH-35105 WG	31.5 + 9 + 4.5	0	0	0	0	0	0
T-17	CH-35105 WG	35 + 10 + 5	1	3	0	1	0	0

DAA – Days after application,

L- Leaf injury on tips/surface, N-Necrosis, V- Vein clearing, E- Epinasty, H- Hyponasty, W-wilting

As seen in Table 8, it can be appreciated that the composition of the present invention is not phytotoxic to various plant parts even though they are more effective against various weeds.

Table 9 Phytotoxic effect of various treatments on wheat crop after 10 DAA

Trial no.	Treatment details	Dose a.i./ha	10 DAA					
			L	N	V	E	H	W
T-1	Untreated	-	-	-	-	-	-	-
T-2	Bispyribac sodium 10 SC	37.5	0	0	0	0	0	0
T-3	Penoxsulam 2.67 OD	25	0	0	0	0	0	0
T-4	Chlorimuron ethyl 25 WP	6	0	0	0	0	0	0
T-5	CH-24124 WG (EX-1)	27 + 13.5 + 5.4	0	0	0	0	0	0
T-6	CH-24124 WG	30 + 15 + 6.0	0	0	0	0	0	0
T-7	CH-24124 WG	33 + 16.5 + 6.6	0	0	0	0	0	0
T-8	CH-20835 WG (EX-2)	25 + 10 + 4.38	0	0	0	0	0	0
T-10	CH-20835 WG	30 + 12 + 5.25	0	0	0	0	0	0

T-11	CH-20835 WG	35 + 14 + 6.13	1	3	0	1	0	0
T-12	CH-30154 WG (EX-3)	30 + 15 + 4	0	0	0	0	0	0
T-13	CH-30154 WG	33 + 16.5 + 4.4	0	0	0	0	0	0
T-14	CH-30154 WG	36 + 18 + 4.8	1	3	0	1	0	0
T-15	CH-35105 WG (EX-4)	28 + 8 + 4	0	0	0	0	0	0
T-16	CH-35105 WG	31.5 + 9 + 4.5	0	0	0	0	0	0
T-17	CH-35105 WG	35 + 10 + 5	1	3	0	1	0	0

DAA – Days after application,

L- Leaf injury on tips/surface, N-Necrosis, V- Vein clearing, E- Epinasty, H- Hyponasty, W-wilting

As seen in Table 9, it can be appreciated that the composition of the present invention is not phytotoxic to various plant parts even though they are more effective against various weeds.

Table: 10. Overall weed control (NLW, SEDGES & BLW) and Phytotoxicity level

Trial no.	Treatment details	Dose a.i./ha	Overall weed control (28 DAA)	Phytotoxicity (0-9 SES)
T-1	Untreated	-	-	-
T-2	Bispyribac sodium 10 SC	37.5	64.37	0
T-3	Penoxsulam 2.67 OD	25	64.93	0
T-4	Chlorimuron ethyl 25 WP	6	52.10	0
T-5	CH-24124 WG (EX-1)	27 + 13.5 + 5.4	80.70	0
T-6	CH-24124 WG	30 + 15 + 6.0	88.03	0
T-7	CH-24124 WG	33 + 16.5 + 6.6	90.27	0
T-8	CH-20835 WG (EX-2)	25 + 10 + 4.38	74.83	0
T-10	CH-20835 WG	30 + 12 + 5.25	77.57	0

T-11	CH-20835 WG	35 + 14 + 6.13	80.43	3
T-12	CH-30154 WG (EX-3)	30 + 15 + 4	72.43	0
T-13	CH-30154 WG	33 + 16.5 + 4.4	79.87	0
T-14	CH-30154 WG	36 + 18 + 4.8	82.17	3
T-15	CH-35105 WG (EX-4)	28 + 8 + 4	74.00	0
T-16	CH-35105 WG	31.5 + 9 + 4.5	79.47	0
T-17	CH-35105 WG	35 + 10 + 5	80.03	3

Note

CH-24124 WG (Bispyribac sodium 24% + Penoxsulam 12% + Chlorimuron ethyl 4.8% WG

CH-20835 WG (Bispyribac sodium 20% + Penoxsulam 8% + Chlorimuron ethyl 3.5% WG

5 CH-30154 WG (Bispyribac sodium 30% + Penoxsulam 15% + Chlorimuron ethyl 4.0% WG

CH-35105 WG (Bispyribac sodium 35% + Penoxsulam 10% + Chlorimuron ethyl 5.0% WG

10 The prominent grassy weed species in the untreated plot at the time of application were *Echinochloa colonum* among the narrow leaved weeds while among the broad leaves weed the major weed flora *Marselia spp.* and Sedges- *Cyperus iria*. The above observational data take into account the same.

I/We Claim:

1. A herbicidal composition comprising a) Bispyribac sodium b) Chlorimuron ethyl or its derivatives and c) Penoxsulam as active ingredients.
- 5 2. The herbicidal composition as claimed in claim 1 further comprising at least one agriculturally acceptable excipient.
- 10 3. The herbicidal composition as claimed in claim 2, wherein said herbicidal composition is formulated as a formulation selected from the group consisting of water-soluble concentrates (SL), emulsifiable concentrates (EC), emulsions (EW), micro-emulsions (ME),
Suspension concentrates (SC), oil-based suspension concentrates (OD), flowable suspensions (FS), water-dispersible granules (WG), water-soluble granules (SG), wettable powders (WP), water soluble powders (SP), granules (GR), encapsulated granules (CG), fine granules (FG), macrogranules (GG), dry flowables (DF), aqueous Suspo-emulsions (SE),
15 capsule suspensions (CS) and microgranules (MG).
- 20 4. The herbicidal composition as claimed in claim 3, wherein said composition is formulated as a wettable granule (WG).
- 25 5. The herbicidal composition as claimed in claim 2, wherein said at least one agriculturally acceptable excipient is selected from the group consisting of at least a wetting agent, at least a dispersing agent, at least a defoaming agent, at least a binder, at least a suitable carrier, and combinations thereof.
- 30 6. The herbicidal composition as claimed in claim 1, wherein Bispyribac sodium is present in an amount ranging from 18 to 40% w/w, Chlorimuron ethyl is present in an amount ranging from 3 to 6% w/w and Penoxsulam is present in an amount ranging from 6 to 25% w/w of the herbicidal composition.
7. The herbicidal composition as claimed in claim 6, wherein Bispyribac sodium is present in an amount of 24%w/w, Chlorimuron ethyl is present in an amount of 4.8%w/w, and Penoxsulam is present in an amount of 12%w/w.

8. The herbicidal composition as claimed in claim 1, wherein said herbicidal composition dosage is in the range of 120-160 gm/ha.

5 9. A method of concurrent control of narrow leaved weeds, broad leaved weeds and sedges in agricultural crops, comprising the steps of:

a. contacting agricultural crop with a herbicidal composition as claimed in claim 1, wherein said composition dosage is in the range of 120-160gm/ha.

10 10. The method as claimed in claim 9, wherein said agricultural crop is rice.

11. The method as claimed in claim 10, wherein contacting herbicidal composition with rice is done 9-14 days post transplanting of rice or 18-24 days post transplanting.

15 12. A process for preparing a herbicidal composition as claimed in claim 4, said process comprising:

- a. preparing a blend of Bispyribac Sodium, Chlorimuron ethyl, Penoxsulam, and suitable agriculturally acceptable excipients to obtain a first pre-mix;
- b. grinding the first pre-mix by jet-milling to obtain a second pre-mix having mean particle size of less than 10 microns;
- c. preparing a dough from the second pre-mix;
- d. subjecting the second pre-mix to an extruder to obtain granules; and
- e. drying the granules to obtain the water-dispersible formulation.
- 20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2022/050404

A. CLASSIFICATION OF SUBJECT MATTER
A01N43/90, A01P13/00 Version=2022.01

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, A01P

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)

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.
X	WO 2016102499 A1 (MITSUI AGRISCIENCE INTERNATIONAL S.A./N.V. ET AL.) 30 June 2016 (30-06-2016) whole document	1-12
Y	WO 2016099802 A1 (DOW AGROSCIENCES LLC[US]) 23 June 2016 (23-06-2016) abstract, page-10, para-5, and claims 1, 7-13	1-12
Y	WO 2019244088 A1 (PI INDUSTRIES LTD[IN]) 26 December 2019 (26-12-2019) abstract, claims 1, 3-4, 8-12	1-12

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

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"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
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Citation	Pub.Date	Family	Pub.Date
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