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(54) Title: BROAD SPECTRUM HERBICIDAL COMPOSITION FOR WHEAT

(57) Abstract: The present invention relates to a combination of herbicides for the control of harmful undesirable plants. In particular, the invention relates to a novel, synergistic and broad-spectrum herbicidal composition for the control of both narrow leaved and broad-leaved weeds in Wheat crop. The invention further discloses a process for preparing said herbicidal composition.

BROAD SPECTRUM HERBICIDAL COMPOSITION FOR WHEAT

FIELD OF INVENTION:

The present invention relates to a combination of herbicides for the control of harmful undesirable plants. In particular, the invention relates to a novel, synergistic and broad-spectrum herbicidal composition for the control of both narrow leaved and broad-leaved weeds in Wheat crop.

BACKGROUND OF THE INVENTION:

Weeds are a persistent problem faced by farmers. If allowed to grow unrestricted, they compete with crop plants and cause enormous yield reductions, increase the irrigation requirement thereby increasing the total cost of agriculture. They further reduce the value of produce and the agricultural land while also causing health hazards to humans and animals.

Many approaches have been designed to tackle the unwanted plants or weeds in agricultural fields. A common approach taken in the recent years is combining of herbicides with varied modes of action which allows broader spectrum of control among other several advantages. However, currently such compositions are limited in numbers and there is a need to develop more pesticidal compositions to help farmers especially in wake of unpredictable weather conditions and complex weed situations faced by them.

There is thus a need in the art for combinations that have multiple advantages to offer such as an herbicidal combination that is synergistic, effective against a broad range of weeds, reduces dosage of herbicides used thus causing minimal damage to the environment and that does not cause any phytotoxicity to the crops.

The three active ingredients used in the present herbicidal composition are well known in the art and have been used both as individual formulations and combinations.

Pinoxaden ([8-(2,6-diethyl-4-methylphenyl)-7-oxo-1,2,4,5-tetrahydropyrazolo[1,2 d][1,4,5]oxadiazepin-9-yl] 2,2-dimethylpropanoate) is a selective post-emergence herbicide for the control of annual grass weeds in cereal crops. Pinoxaden belongs to the phenylpyrazole class of herbicides which acts by inhibiting the enzyme acetyl-CoA carboxylase (ACCase), thereby preventing fatty acid synthesis. It is applied as a foliar spray and is absorbed and translocated throughout the plant. Weeds treated with pinoxaden will begin to show leaf chlorosis and yellowing at the nodes within days of treatment beginning, and decay and necrosis follows.

Metribuzin (4-amino-6-tert-butyl-3-(methylthio)-1,2,4-triazin-5(4H)-one) is an herbicide used both as pre- and post-emergence herbicide in crops including soy bean, potatoes, tomatoes and sugar cane. It is a triazinone herbicide that inhibits photosynthesis in a susceptible plant by binding to a protein of the photosystem II complex which in turn causes a chain of events where eventually plant lipids and proteins are attacked and oxidized by highly reactive free radicals. As a result, chlorophyll and plant pigments are lost causing chlorosis followed by plant cell dying and disintegration.

Metsulfuron-methyl (methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-ylcarbamoylsulfamoyl)benzoate is a sulfonylurea herbicide used to control broadleaf weeds and some annual grasses. It is a systemic herbicide with foliar and soil activity and works rapidly after it is taken up by the plant. It acts by inhibiting cell division in the shoots and roots of the plant, and it is biologically active at low use rates. The most common uses of metsulfuron-methyl include on crops like wheat, barley, rye, and pastures. Because it has residual activity in soils, it is necessary to allow ample time for the chemical to break down before planting certain crops.

Although, combination of herbicides are designed to control broad spectrum of weeds, there is no certainty that such combination will deliver the desired results. Many a times, combinations of herbicides lead to simply additive effects or antagonistic effects. An incompatible combination may also result to phytotoxicity in the crop plants. Scientists must therefore be careful while selecting the herbicides that can be combined to offer a synergistic effect that would control weeds effectively without any phytotoxicity on the crop and toxicity to the ecosystem.

OBJECTS OF THE INVENTION:

An object of the present invention is to provide a novel herbicidal combination and composition which is free from the existing drawbacks of the prior art, especially in controlling the management of resistance, a process for producing the combination and uses of the combination and composition.

SUMMARY OF THE INVENTION:

The present invention relates to a novel, synergistic herbicidal combination and a composition comprising the combination for control of a broad spectrum of both narrow-leaved and broad-leaved weeds in agricultural crops, particularly Wheat (*Triticum aestivum*)

In particular, the present invention relates to an herbicidal combination comprising Pinoxaden as first active ingredient, Metribuzin as the second active ingredient and Metsulfuron methyl as the third active ingredient. The combination contains the actives in specific weight percentages. The combination of the present invention may be present along with at least one agriculturally acceptable excipient. The present invention further relates to a process for preparation of said novel, synergistic, broad spectrum herbicidal composition and uses thereof.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 illustrates the flow diagram representation of the steps in preparation of WG formulation of present herbicidal composition.

DETAILED DESCRIPTION OF THE 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 any and all combinations of any two or more of said steps 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 serial 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 particular 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 "agrochemical 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 is drawn to a synergistic herbicidal combination comprising:

(a) A first active ingredient which is Pinoxaden;
(b) A second active ingredient which is Metribuzin; and
(c) A third active ingredient which is Metsulfuron methyl.

The present invention provides a unique combination, wherein the actives interact in such a manner to impart surprising herbicidal properties. Neither the combination nor its unexpected weedicide property are identified or even envisaged by a skilled person in the art and can never be in the domain of routine experimentation.

In an aspect present invention relates to a novel, synergistic, broad spectrum herbicidal combination comprising of a) Pinoxaden in an amount ranging from 2 to 12 % w/w of the herbicidal composition b) Metribuzin in an amount ranging from 10 to 50 % w/w of the herbicidal composition c) Metsulfuron methyl in an amount ranging from 0.1 to 20 % w/w of the herbicidal composition.

The combination of the present invention utilizes the Actives in the strength of Pinoxaden at 6.5%, Metribuzin at 17% and Metsulfuron methyl at 0.53%.

Without being limited by theory, it was observed by the inventors that the herbicidal composition of the present invention provides a superior and broader spectrum of weed control at much lower levels of active ingredient combination as compared to what is achieved when the active ingredients are applied alone as illustrated in the present invention by way of examples.

In an embodiment, the present invention discloses a herbicidal composition, comprising the combination of the present invention along with agriculturally acceptable excipient selected from the group comprising a wetting agent, dispersing agent, a binder, carrier, antifoaming agent, etc.

The dispersing agent of the composition of the present invention, may be selected from the group comprising sodium lignosulphonates, sodium naphthalene sulphonate- formaldehyde condensates, aliphatic alcohol ethoxylates, tristyrylphenol ethoxylates and esters, ethylene oxide/propylene oxide block copolymers. Preferably the dispersing agent is Sodium salt of naphthalene sulfonate condensate.

The antifoaming agent, of the present composition may be selected from the group comprising silicones, silica, waxes,fatty alcohols . preferably the antifoaming agent is

The wetting agent, of the present composition may be selected from the group comprising blend of alkyl naphthalene sulfonate, sodium salt, Sodium laurel sulphate. In a preferred embodiment, the wetting agent is Sodium laurel sulphate.

The present composition may comprise one or more carriers, selected from the group comprising Dextrose, Lactose, Soluble starch, Galactose, Amylodextrin, Maltose, Mannitol, Sucrose, Sorbitol and China clay.

The present composition may comprises one or more binders, wherein said binder may be selected from the group comprising Starch paste, Hydroxypropyl methylcellulose (HPMC), Polyvinyl Pyrrolidone (PVP), Lactose monohydrate. In a preferred embodiment, said binder is lactose monohydrate.

In an embodiment, said Dispersing agent is present in an amount ranging from 3 to 8% w/w of the composition.

In an embodiment, said Wetting-agent is present in an amount ranging from 1 to 4% w/w of the composition.

In an embodiment, said anti- foaming agent is present in an amount ranging from 00.01-0.1% w/w of the composition.In an embodiment, said carrier is present in an amount ranging from 3 to 10% w/w of the composition .

The herbicidal composition of the present invention may be formulated in a form selected from the group comprising Wettable granules (WG), Water-soluble granules (SG), Wettable powders (WP), Water soluble powders (SP), Granules (GR), Encapsulated granules (CG), Fine granules (FG), Macrogranules (GG), Microgranules (MG), suspensions, emulsions, aqueous suspensions, etc.. In a preferred embodiment the herbicidal composition may be formulated as wettable granules (WG).

The herbicidal composition of the present invention is formulated in a form of wettable granule. In an embodiment, the wettable granules (WG) of the present invention comprise a wetting agent, a dispersing agent, a defoaming agent, a binder and a suitable carrier.

In another embodiment, the present invention discloses a process for preparing a combination or a composition of the present invention comprising the steps of:

i) Adding at least one wetting agent, dispersing agent, filler and Pinoxaden technical and mixing to obtain a homogeneous mix.
ii) Adding metribuzin technical and metsulfuron methyl to the mixture of step (i).
iii) Adding rest of the adjuvants to the mixture of step (ii) to obtain a homogeneous mass.
iv) Blending the homogeneous mass obtained in step (iii).
v) Grinding the homogenous mass obtained in step (iv) until a mean particle size in the range of 1-10 micron is obtained.
vi) Again blending the mass obtained in step (v) (Post mixing blending) to obtain a homogeneous mass.
vii) Preparing the dough by taking the homogenous mass obtained in step (vi)
viii) Preparing granules through an extruder.
ix) Drying the granules obtained in step (viii) in hot air oven to obtain the wettable granules (WG)

In an embodiment, the combination and the composition of the present invention may be utilized as synergistic and broad-spectrum herbicidal combination and composition for control of both narrow leaved weeds and broad leaved weeds in agricultural crops, particularly Wheat and for delaying resistance

It has been found that the combination and the composition of the present invention effectively controls narrow leaved weeds *Phalaris minor* and *Avena ludoviciana* and broad leaved weeds controlled by the present herbicidal composition include but are not limited to *Chenopodium album, Rumex spp., Melilotus spp., Fumaria parviflora, Vicia sativa, Anagalis arvensis, Coronopus didymus, Lathyrus spp., Solanum nigrum.*

Advantages of the combination and composition of the present invention:

1. The combination and composition of the present invention delays the development of resistance in the crops.
2. The combination and composition are highly effective in controlling the target weeds in agricultural crops, particularly Wheat.
3. The combination and composition are highly effective in controlling a broad spectrum of both narrow leaved and broad-leaved weeds in agricultural crops, particularly Wheat.
4. The combination and composition are environmentally safe and causes no or negligible phytotoxicity in agricultural crops, particularly wheat.

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: Combination and Preparation of herbicidal composition:

In a preferred embodiment, the tentative composition of the present herbicidal composition is given below:

Table 1: Composition of WG herbicidal composition:

Ingredient	Percentage w/w F1
Pinoxaden technical (Basis of 100.0%)	06.50%
Metribuzin technical (Basis of 100.0%)	17.00%
Metsulfuron technical	00.53%
Sodium bi-carbonate	01.00%
Citric acid	00.50%

Dispersing agent (sodium salt of naphthalene sulfonate condensate)	05.00%
Wetting agent (sodium laurel sulphate)	02.00%
Antifoam	00.05%
PPT Silica	05.00%
China clay	QS to make %
Total quantity	100% w/w

The desired quantity of the active ingredients and adjuvants 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. Fig 1 shows a flow diagram representation of the steps involved in the preparation of the WG the Formulation F1 was tested for quality parameters as per the standard protocols and, the important quality parameters are listed below:

Table 2 (a): Quality parameters of WG formulation

Parameter	**Desired quality**
Description/ physical appearance	The material shall consist of dry, free flowing granules, which shall wet on mixing with water, thereby resulting into a solution suitable for spray. The material shall be free from visible extraneous matter
A.I. Content-	Metribuzin -17% m/m (±5%) Pinoxaden -08% m/m (+5, -3%) Metsulfuron -0.53% m/m (±10%)
Persistence of foaming	Not more than 60 ml after 1 min
Wettability	Max. for 120 secs
Suspensibility	Min 60%
Acidity as H_2SO_4	0.5% max

Table 2 (b): Composition of EC herbicidal formulation

S.No.	Ingredient	Content % w/w
1.	Penoxadin Technical (100% Basis)	06.50%
2.	Metribuzin Technical (100% Basis)	17.00%
3.	Metsulfuron Methyl Technical (100% Basis)	00.53%
4.	Non ionic / Anionic surfactant emulsifier (A: Blend of sulphonated and ethoxylated hydrocarbons) (B: Blend of sulphonated and ethoxylated hydrocarbons)	12.00%
5.	NMP (co solvent)	15.00%
6.	DMSO (co solvent)	15.00%
7	C-9 (solvent)	Q.S.to make
	Total	**100.00 w/w**

The desired quantity of the active metribuzin and DMSO and NMP were weighed and dissolved. After this rest actives and adjuvant were added and mixed in a vessel. The mixing was running 30 min @ 1000rpm.The mixed mass were then checked for quality parameter.

Fig 1 shows a flow diagram representation of the steps involved in the preparation of the EC.

For better comprehension of the present invention, the important quality parameters are listed below.

Table 2(c): Quality parameters of EC formulation

Parameter	**Desired quality**
Description/ physical appearance	Yellow light clear transparent liquid
A.I. Content-	Metribuzin -17% m/m (±5%) Pinoxaden -08% m/m (+5, -3%) Metsulfuron -0.53% m/m (±10%)
Persistence of foaming	Not more than 60 ml after 1 min

PH range	6-8
Emulsion stability	Emulsion remains stable after 60 min

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

The presently disclosed herbicidal trimix (coded as CH-65175) was tested for its bioefficacy against both the narrow leaved and broad-leaved weeds on Wheat crop. The trial was conducted in Karnal on the Wheat variety PBW-343 during Rabi season 2019. The plants were aligned in a plot size of 50 sq. meter, with the spacing of 10 cm between individual crop plants and a spacing of 10 cm between the rows. The trial was laid out in a random block design consisting of a total of 7 treatments in three replications. The trial was conducted at a temp. of 11°C under 75% relative humidity, no winds and under optimum soil moisture conditions. The application of the herbicidal trimix was carried out at the post emergence stage ie. 35 days after sowing of the crop and at 2-4 leaves stage of the emergent weeds.

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 solution.

Table 3 below provides the treatment details of the wheat crop in the trial experiment conducted. For purposes of convenience, the present composition has been represented by the code "CH-65175 WG"

Table 3: Treatment details

Treat	Treatment details	Dose a.i./hectare	Dose/hectare
T-1	Untreated	-	-
T-2	Pinoxaden 5.1 EC	45.9	900 ml
T-3	Metribuzin 70 WP	147	210 g
T-4	Metsulfuron methyl 20 WP	4	20 g
T-5	CH-65175 WDG	45.5+119+3.71	700 g
T-6	CH-65175 WDG	48.75+127.5+3.98	750 g

T-7	CH-65175 WDG	52+136+4.24	800 g
T-8	CH-4251 WDG	28 + 175 + 7	700 g
T-9	CH-4251 WDG	30 + 187.5 + 7.5	750 g
T-10	CH-4251 WDG	32 + 200 +8	800 g
T-11	CH-8252 WDG	24 + 75 + 6	300 g
T-12	CH-8252 WDG	32 + 100 + 8	400 g
T-13	CH-8252 WDG	40 + 125 + 10	500 g
T-14	CH-12175 WDG	84 + 119 + 3.71	700 g
T-15	CH-12175 WDG	90 + 127.5 + 3.98	750 g
T-16	CH-12175 WDG	96 + 136 + 4.24	800 g

Note

CH-65175 WDG (Pinoxaden 6.5% + Metribuzin 17% + Metsulfuron methyl 0.53 WDG

CH-4251 WDG (Pinoxaden 4.0% + Metribuzin 25% + Metsulfuron methyl 1% WDG

CH-8252 WDG (Pinoxaden 8.0% + Metribuzin 25% + Metsulfuron methyl 2% WDG

CH-12175 WDG (Pinoxaden 12% + Metribuzin 17% + Metsulfuron methyl 0.53% WDG

From the experiments 48.75+127.5+3.98 gm ai/hectare was shown to provide effective control of both the narrow leaved weeds and broad-leaved weeds at 2-4 leaved stage of weeds without any phytotoxicity on wheat crop.

Example 2 (a) EVALUATION OF BIOEFFICACY IN WHEAT CROP

Weed count: A quadrate of the dimensions (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 percent weed control was determined based on no. of live weed flora at 14 and 28 days after application as per following:

$$\textbf{Percent weed control} = \frac{WC - WT}{\ldots\ldots\ldots\ldots} \times 100$$

WC

Where WC = No. of weed in control plot

WT = No. of weed in treated plot

Observations

Table 4 (a): Effect of herbicidal treatment on weed density of narrow & Broad leaves weeds at 14DAA

Treatments	Dose (a.i/ha)	Percent control of Narrow leaves & Broad weeds (Mean 0.25 sqm) over UTC					
		Phalaris minor		*Chenopodium album*		*Fumaria spp.*	
		Live pop.	% Control	Live pop.	% Control	Live pop.	% Control
Untreated	-	19.5	-	10	-	8.5	-
Pinoxaden 5.1 EC	45.9	10.3	47.66	9.5	5.0	9.5	0.00
Metribuzin 70 WP	147	12.4	36.41	4.5	55.0	2.5	70.58
Metsulfuron methyl 20 WP	4	17.2	11.79	3.5	65.0	3.0	64.70
Pinoxaden 6.5% + Metribuzin 17% WG	48.75 + 127.5	5.5	71.79	4.5	55.0	3.0	64.70
Pinoxaden 6.5% + Metsulfuron methyl 0.53 WG	48.75 + 3.98	13.0	33.33	6.0	40.0	4.5	47.05
Metribuzin 17% + Metsulfuron methyl 0.53% WG	127.5 + 3.98	18.5	5.12	5.5	45.0	2.0	76.47
CCP-65175 WG	48.75+127.5 +3.98	1.5	92.30	0.0	100	0.0	100

Table 4 (b): Effect of herbicidal treatment on weed density of Narrow& Broad leaves weeds at 28 DAA

Treatments	Dose (a.i/ha)	Percent control of Narrow leaves & Broad weeds (Mean 0.25 sqm) over UTC					
		Phalaris minor		*Chenopodium album*		*Fumaria spp.*	
Untreated	-	Live pop.	% Control	Live pop.	% Control	Live pop.	% Control
Pinoxaden 5.1 EC	45.9	26.0	-	14	-	9.0	-
Metribuzin 70 WP	147	12.0	53.84	4.5	67.85	3.0	66.66
Metsulfuron methyl 20 WP	4	23.0	11.53	2.5	82.14	4.5	50.0
Pinoxaden 6.5% + Metribuzin 17% WG	48.75 + 127.5	9.5	63.46	5.0	64.28	3.0	66.66
Pinoxaden 6.5% + Metsulfuron methyl 0.53 WG	48.75 + 3.98	14.0	46.15	6.5	53.57	3.5	61.11
Metribuzin 17% + Metsulfuron methyl 0.53% WG	127.5 + 3.98	19.0	26.92	2.0	85.71	2.5	72.22
CCP-65175 WG	48.75+127.5 +3.98	4.5	82.69	1.5	89.23	1.0	88.88

Table 4 (c): Effect of herbicidal treatment on weed density of Narrow & Broad-leaved weeds at 14 DAA

Treatments	**Dose (a.i/ha)**	**Percent control of Narrow leaves & Broad weeds (Mean 0.25 sqm) over UTC**		
		Phalaris minor	***Chenopodium album***	***Fumaria spp.***

		Live pop.	%control	Live pop.	%control	Live pop.	%control
Untreated	-	21	-	12	-	10	-
Pinoxaden 5.1 EC	45.9	10.5	50.0	11	8.33	8.0	20.0
Metribuzin 70 WP	147	15.0	28.57	6.0	50.0	2.0	80.0
Metsulfuron methyl 20 WP	4	19.0	9.52	4.0	66.67	2.0	90.0
CH-65175 WDG	45.5+119+3.71	3.0	85.71	2.0	83.33	1.0	90.0
CH-65175 WDG	48.75+127.5+3.98	2.0	90.48	1.5	87.50	0.5	95.0
CH-65175 WDG	52+136+4.24	1.0	95.24	1.5	87.50	0.5	95.0
CH-4251 WDG	28 + 175 + 7	9.0	57.14	2.0	83.33	1.0	90.0
CH-4251 WDG	30 + 187.5 + 7.5	8.0	61.90	0.0	100.0	0.0	100.0
CH-4251 WDG	32 + 200 +8	7.0	66.67	0.0	100.0	0.0	100.0
CH-8252 WDG	24 + 75 + 6	10.0	52.38	7.5	37.50	0.0	100.0
CH-8252 WDG	32 + 100 + 8	8.0	61.90	6.0	50.0	0.0	100.0
CH-8252 WDG	40 + 125 + 10	8.5	59.52	6.0	50.0	0.0	100.0
CH-12175 WDG	84 + 119 + 3.71	2.0	90.48	2.0	83.33	1.0	90.0
CH-12175 WDG	90 + 127.5 + 3.98	2.0	80.95	1.5	87.50	0.5	95.0
CH-12175 WDG	96 + 136 + 4.24	1.0	93.33	1.5	87.50	0.5	95.0

Table 4(d): Effect of herbicidal treatment on weed density of Narrow& Broad leaved weeds at 28 DAA

Treatment	Dose (a.i/ha)	Percent control of Narrow leaves & Broad weeds (Mean 0.25 sqm) over UTC					
		Phalaris minor		*Chenopodium album*		*Fumaria spp.*	
		Live pop.	%control	Live pop.	%control	Live pop.	%control
Untreated	-	27	-	12	-	10	-
Pinoxaden 5.1 EC	45.9	13.5	50.0	11	8.33	8.0	20.0
Metribuzin 70 WP	147	17.0	37.04	6.0	50.0	2.0	80.0
Metsulfuron methyl 20 WP	4	19.0	29.63	4.0	66.6	2.0	80.0
CH-65175 WDG (Example-1)	45.5+119+3.71	4.0	85.19	4.0	66.6	2.0	80.0
CH-65175 WDG	48.75+127.5+3.98	3.0	88.89	1.5	87.5	1.0	90.0
CH-65175 WDG	52+136+4.24	2.0	92.59	0.0	100	1.0	90.0
CH-4251 WDG (Example-2)	28 + 175 + 7	14.0	48.15	1.0	91.67	1.0	90.0
CH-4251 WDG	30 + 187.5 + 7.5	12.0	55.56	1.0	91.67	0.0	100.0
CH-4251 WDG	32 + 200 +8	10.0	62.96	0.0	100.0	0.0	100.0
CH-8252 WDG (Example-3)	24 + 75 + 6	15.0	44.44	8.5	29.17	3.0	70.0
CH-8252 WDG	32 + 100 + 8	13.0	51.85	7.0	41.67	2.0	80.0

CH-8252 WDG	40 + 125 + 10	12.5	53.70	6.5	45.83	1.0	90.0
CH-12175 WDG (Example-4)	84 + 119 + 3.71	4.0	85.19	4.0	66.6	2.0	80.0
CH-12175 WDG	90 + 127.5 + 3.98	3.0	88.89	1.5	87.5	1.0	90.0
CH-12175 WDG	96 + 136 + 4.24	2.0	92.59	0.0	100	1.0	90.0

Example 3: Evaluation of phytotoxicity of the present herbicidal composition

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

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-6(a) Study conducted to assess the phytotoxic effect after various treatments on wheat crop at 3 DAA.

Treatments	Treatment details	Dose a.i./hectare	3 DAA					
			L	N	V	E	H	W
T-1	Untreated	-	-	-	-	-	-	-
T-2	Pinoxaden 5.1 EC	45.9	*0*	*0*	*0*	*0*	*0*	*0*
T-3	Metribuzin 70 WP	147	*1*	*1*	*0*	*0*	*0*	*0*
T-4	Metsulfuron methyl 20 WP	4	*0*	*0*	*0*	*0*	*0*	*0*
T-5	CH-65175 WDG	45.5+119+3.71	*0*	*0*	*0*	*0*	*0*	*0*
T-6	CH-65175 WDG	48.75+127.5+3.98	*0*	*0*	*0*	*0*	*0*	*0*
T-7	CH-65175 WDG	52+136+4.24	*0*	*0*	*0*	*0*	*0*	*0*
T-8	CH-4251 WDG	28 + 175 + 7	*0*	*0*	*0*	*0*	*0*	*0*
T-10	CH-4251 WDG	30 + 187.5 + 7.5	*3*	*1*	*0*	*0*	*0*	*0*
T-11	CH-4251 WDG	32 + 200 +8	*3*	*1*	*0*	*0*	*0*	*0*
T-12	CH-8252 WDG	24 + 75 + 6	*0*	*0*	*0*	*0*	*0*	*0*
T-13	CH-8252 WDG	32 + 100 + 8	*0*	*0*	*0*	*0*	*0*	*0*
T-14	CH-8252 WDG	40 + 125 + 10	*0*	*0*	*0*	*0*	*0*	*0*
T-15	CH12175 WDG	84 + 119 + 3.71	*0*	*0*	*0*	*0*	*0*	*0*
T-16	CH-12175 WDG	90 + 127.5 + 3.98	*3*	*1*	*0*	*0*	*0*	*0*
T-17	CH-12175 WDG	96 + 136 + 4.24	*3*	*1*	*0*	*0*	*0*	*0*

DAA – Days after application,

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

Table 6 (b) Study conducted to assess the phytotoxic effect of various treatments on wheat crop at 7 DAA

Treatments	Treatment details	Dose a.i./hectare	7 DAA					
			L	N	V	E	H	W
T-1	Untreated	-	-	-	-	-	-	-
T-2	Pinoxaden 5.1 EC	45.9	*0*	*0*	*0*	*0*	*0*	*0*
T-3	Metribuzin 70 WP	147	*3*	*1*	*0*	*0*	*0*	*0*
T-4	Metsulfuron methyl 20 WP	4	*0*	*0*	*0*	*0*	*0*	*0*
T-5	CH-65175 WDG	45.5+119+3.71	*0*	*0*	*0*	*0*	*0*	*0*
T-6	CH-65175 WDG	48.75+127.5+3.98	*0*	*0*	*0*	*0*	*0*	*0*
T-7	CH-65175 WDG	52+136+4.24	*0*	*0*	*0*	*0*	*0*	*0*
T-8	CH-4251 WDG	28 + 175 + 7	*0*	*0*	*0*	*0*	*0*	*0*
T-10	CH-4251 WDG	30 + 187.5 + 7.5	*3*	*1*	*0*	*0*	*0*	*0*
T-11	CH-4251 WDG	32 + 200 +8	*3*	*1*	*0*	*0*	*0*	*0*
T-12	CH-8252 WDG	24 + 75 + 6	*0*	*0*	*0*	*0*	*0*	*0*
T-13	CH-8252 WDG	32 + 100 + 8	*0*	*0*	*0*	*0*	*0*	*0*
T-14	CH-8252 WDG	40 + 125 + 10	*0*	*0*	*0*	*0*	*0*	*0*
T-15	CH-12175 WDG	84 + 119 + 3.71	*0*	*0*	*0*	*0*	*0*	*0*
T-16	CH-12175 WDG	90 + 127.5 + 3.98	*3*	*1*	*0*	*0*	*0*	*0*
T-17	CH-12175 WDG	96 + 136 + 4.24	*3*	*1*	*0*	*0*	*0*	*0*

DAA – Days after application,

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

Table 6 (c) Study conducted to assess the phytotoxic effect of various treatments on wheat crop at 10 DAA

Treatments	Treatment details	Dose a.i./hectare	10 DAA					
			L	N	V	E	H	W
T-1	Untreated	-	-	-	-	-	-	-
T-2	Pinoxaden 5.1 EC	45.9	*0*	*0*	*0*	*0*	*0*	*0*
T-3	Metribuzin 70 WP	147	*3*	*1*	*0*	*0*	*0*	*0*
T-4	Metsulfuron methyl 20 WP	4	*0*	*0*	*0*	*0*	*0*	*0*
T-5	CH-65175 WDG	45.5+119+3.71	*0*	*0*	*0*	*0*	*0*	*0*
T-6	CH-65175 WDG	48.75+127.5+3.98	*0*	*0*	*0*	*0*	*0*	*0*
T-7	CH-65175 WDG	52+136+4.24	*0*	*0*	*0*	*0*	*0*	*0*
T-8	CH-4251 WDG	28 + 175 + 7	*0*	*0*	*0*	*0*	*0*	*0*
T-10	CH-4251 WDG	30 + 187.5 + 7.5	*3*	*1*	*0*	*0*	*0*	*0*
T-11	CH-4251 WDG	32 + 200 +8	*3*	*1*	*0*	*0*	*0*	*0*
T-12	CH-8252 WDG	24 + 75 + 6	*0*	*0*	*0*	*0*	*0*	*0*
T-13	CH-8252 WDG	32 + 100 + 8	*0*	*0*	*0*	*0*	*0*	*0*
T-14	CH-8252 WDG	40 + 125 + 10	*0*	*0*	*0*	*0*	*0*	*0*
T-15	CH-12175 WDG	84 + 119 + 3.71	*0*	*0*	*0*	*0*	*0*	*0*
T-16	CH-12175 WDG	90 + 127.5 + 3.98	*3*	*1*	*0*	*0*	*0*	*0*
T-17	CH-12175 WDG	96 + 136 + 4.24	*3*	*1*	*0*	*0*	*0*	*0*

DAA – Days after application,

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

Table: 6(d) Overall weed control (Both NLW & BLW) and Phytotoxicity level.

Treatments	Treatment details	Dose a.i./hectare	Overall weed control (28 DAA)	Phytotoxicity (0-9 SES)
T-1	Untreated	-	-	-
T-2	Pinoxaden 5.1 EC	45.9	26.11	*0*
T-3	Metribuzin 70 WP	147	55.68	*3*
T-4	Metsulfuron methyl 20 WP	4	58.74	*0*
T-5	CH-65175 WDG (Example-1)	45.5+119+3.71	77.26	*0*
T-6	CH-65175 WDG	48.75+127.5+3.98	88.80	*0*
T-7	CH-65175 WDG	52+136+4.24	94.20	*0*
T-8	CH-4251 WDG (Example-2)	28 + 175 + 7	76.61	*0*
T-10	CH-4251 WDG	30 + 187.5 + 7.5	82.41	*3*
T-11	CH-4251 WDG	32 + 200 +8	87.65	*3*
T-12	CH-8252 WDG (Example-3)	24 + 75 + 6	47.87	*0*
T-13	CH-8252 WDG	32 + 100 + 8	57.84	*0*
T-14	CH-8252 WDG	40 + 125 + 10	63.18	*0*
T-15	CH-12175 WDG (Example-4)	84 + 119 + 3.71	77.26	*0*
T-16	CH-12175 WDG	90 + 127.5 + 3.98	88.80	*3*
T-17	CH-12175 WDG	96 + 136 + 4.24	94.20	*3*

Note

CH-65175 WDG (Pinoxaden 6.5% + Metribuzin 17% + Metsulfuron methyl 0.53 WDG

CH-4251 WDG (Pinoxaden 4.0% + Metribuzin 25% + Metsulfuron methyl 1% WDG

CH-8252 WDG (Pinoxaden 8.0% + Metribuzin 25% + Metsulfuron methyl 2% WDG

CH-12175 WDG (Pinoxaden 12% + Metribuzin 17% + Metsulfuron methyl 0.53% WDG

Result & Conclusions:

The prominent grassy weed species in the weedy plot at the time of application were *Phalaris minor in the narrow leaved weeds while among the broad leaves weed the major weed flora included Chenopodium album and Fumaria spp.*

As shown in the above data, application of the novel herbicidal composition coded as CH-65175 WG (Pinoxaden 6.5% + Metribuzin 17% + Metsulfuron methyl 0.53 % WG) at a dosage range of 45.5+119+3.71 gm a.i./hectare to 48.75+127.5+3.98 gm ai/hectare was shown to provide effective control of both the narrow leaved weeds and broad-leaved weeds at 2-4 leaved stage of weeds without any phytotoxicity on wheat crop. The combination of the present invention is synergistic and provides enhanced efficacy in controlling weeds in comparison to individual in comparison with the individual components or a combination of two actives.

We Claim:

1) A synergistic herbicidal combination comprising:

(a) A first active ingredient which is Pinoxaden;

(b) A second active ingredient which is Metribuzin; and

(c) A third active ingredient which is Metsulfuron methyl.

2) The herbicidal combination as claimed in claim 1, wherein the amount of Pinoxaden ranges from 2-12% w/w, the amount of Metribuzin ranges from 10-50% w/w, and the amount of Metsulfuron methyl ranges from 01-20% % w/w.

3) The herbicidal combination as claimed in claim 1, wherein the strength of the Pinoxaden is 6.5%, Metribuzin is 17% and Metsulfuron methyl at 0.53%.

4) An herbicidal composition comprising the combination as claimed in claim 1, along with agriculturally acceptable excipients.

5) The herbicidal composition as claimed in claim 4, wherein said herbicidal composition further comprises agriculturally acceptable excipients selected from the group comprising at least an anti-freezing agent, at least a surfactant, at least a dispersing agent, at least a wetting agent, at least a defoamer, at least a thickener, at least an antibacterial agent, demineralized water, and combinations thereof.

6) The herbicidal composition as claimed in claim 4, wherein said at least one dispersing agent that is present in an amount ranging from 3-8% w/w, at least one wetting agent that is present in an amount ranging from 1-4% w/w, at least one antifoaming agent that is present in an amount ranging from 00.01-0.1% w/w, at least one carrier that is present in an amount ranging from 3-10% w/w, at least one filler that is present in an amount ranging from 0.2-2% w/w and water to make up the volume to 100% w/w.

7) The herbicidal composition as claimed in claim 4, wherein said herbicidal composition is formulated in a form selected from the group consisting of emulsifiable concentrate (EC) wettable powder (WP), soluble (Liquid) concentrate (SL), Soluble powder (SP), Capsule

suspension (CS) Water dispersible granules (WDG), Micro-emulsions (ME), Wettable granules (WG) and Suspension concentrate (SC).

8) The herbicidal composition as claimed in claim 4, wherein the said herbicidal composition is Wettable granules (WG).

9) A process for preparing the synergistic herbicidal composition as claimed in claim 4, said process comprising the following steps:

- **i)** Adding at least one wetting agent, dispersing agent, filler and Pinoxaden technical and mixing to obtain a homogeneous mix;
- **ii)** Adding metribuzin technical and metsulfuron methyl to the mixture of step (i);
- **iii)** Adding rest of the adjuvants to the mixture of step (ii) to obtain a homogeneous mass;
- **iv)** Blending the homogeneous mass obtained in step (iii);
- **v)** Grinding the homogenous mass obtained in step (iv) until a mean particle size in the range of 1-10 micron is obtained;
- **vi)** Again blending the mass obtained in step (v) (Post mixing blending) to obtain a homogeneous mass;
- **vii)** Preparing the dough by taking the homogenous mass obtained in step (vi);
- **viii)** Preparing granules through an extruder;
- **ix)** Drying the granules obtained in step (viii) in hot air oven to obtain the wettable granules (WG).

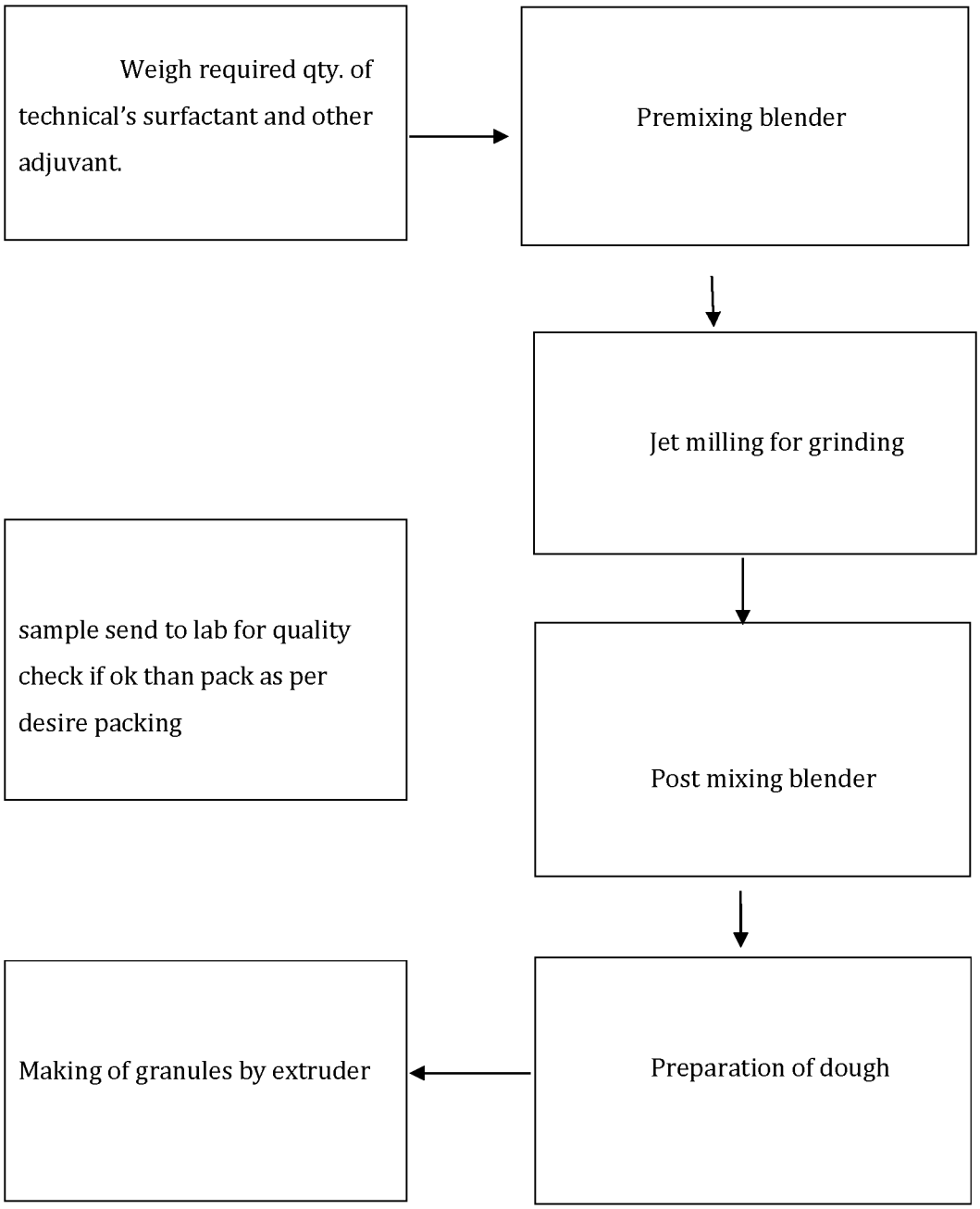
Weigh required qty. of technical's surfactant and other adjuvant.
Premixing blender
Jet milling for grinding
Post mixing blender
Preparation of dough
Making of granules by extruder
sample send to lab for quality check if ok than pack as per desire packing

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2021/051058

A. CLASSIFICATION OF SUBJECT MATTER
A01N47/00,A01N43/90 Version=2021.01

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 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.
Y	US 2021030004 A1 (UPL LTD[IN]) 4 February 2021 (04-02-2021) abstract, page-4, para-0092, page-5, paras-0116, 0120-0126, claims-1, 3	1-9
Y	Combination of pinoxaden with other herbicides against complex weed flora in wheat, Pawan Katara ET AL. Indian Journal of Weed Science 44(4): 225-230, 2012 abstract, pages-226-229, tables-1-5	1-9

☐ 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
20-12-2021	20-12-2021

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/IN2021/051058

Citation	Pub.Date	Family	Pub.Date
US 2021030004 A1	04-02-2021	IN 201831003482 A	02-08-2019
		WO 2019150233 A1	08-08-2019
		EP 3745863 A1	09-12-2020
		CN 111741682 A	02-10-2020