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(54) Title: HERBICIDAL COMBINATIONS

(57) Abstract: The present invention discloses a herbicidal combination comprising a) pyrimidinyl benzoate derivative, and b) imidazolinone derivative. Further, the present invention discloses a synergistic herbicidal combination of bispyribac or bispyribac-sodium and imazethapyr, compositions thereof, process for preparing the composition and method for controlling undesirable plants and weeds by using the synergistic herbicidal combination of the present invention.

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Title of the Invention: HERBICIDAL COMBINATIONS

FIELD OF THE INVENTION:

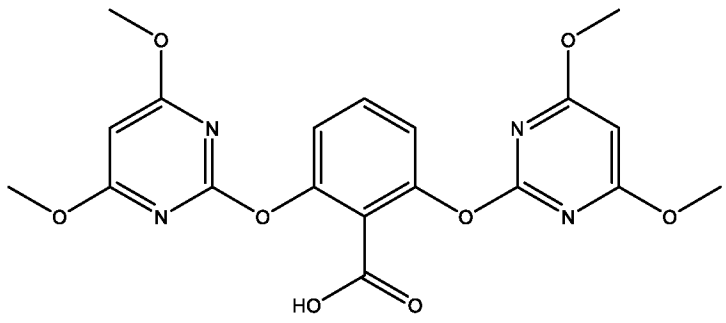
The present invention relates to a herbicidal combination. More particularly, the present invention relates to a synergistic herbicidal combination comprising a) a pyrimidinyl benzoate derivative; and b) an imidazolinone derivative. Further, the present invention relates to a synergistic herbicidal combination which is used for controlling undesirable plants and weeds.

BACKGROUND OF THE INVENTION:

Weeds are undesirable plants that can severely damage yield in crops. Further, weeds are a persistent problem that needs constant monitoring. In routine practice farmers usually control these plants at the pre-plant stage as well as after sowing or both depending on the weed type and the level of infestation. Modern herbicides are used to either control or suppress these undesirable plants so as to allow sown crops a greater share of nutrients. Profitable crop production depends on effective weed control.

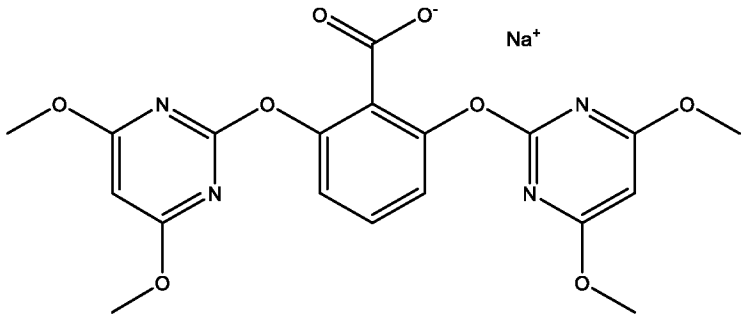
The activity of herbicides can be enhanced in various ways to achieve maximum benefit. One of the ways for effective control can be achieved by selective herbicides which kill certain target weeds while leaving the desired crop relatively unharmed while non-selective herbicides kill both the weeds and crops. Another practice includes combining herbicides that have different modes of action, which allows for a broader spectrum of control and allow for resistance management. Current combinations used for weed management do not effectively handle resistant and persistent weeds. Therefore, there is a need in the art for improved combinations with enhanced efficacy and a broader spectrum of weed control.

Bispyribac acts by the inhibition of the branched amino acid biosynthesis. Its chemical name is 2,6-bis((4,6-dimethoxypyrimidin-2-yl)oxy)benzoic acid, which has the following structure:



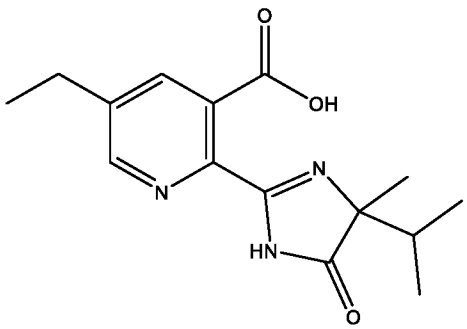
Exemplary uses of bispyribac are described in The Pesticide Manual, Fifteenth Edition, 2009 and include, but are not limited to, control of many grasses, sedges, and broadleaf weeds, especially *Echinochloa* spp., in direct-seeded rice and transplanted rice as well to stunt growth of weeds in non-crop situations. Exemplary chemical forms of bispyribac include, for example, bispyribac-sodium which is a post-emergence pyrimidinyl carboxy herbicide for the control of a wide range of weeds, in particular on *Echinochloa crusgalli*; the application done from the fourth unfolded leaf up to the tillering

stage presents a good plant compatibility in direct-seeded rice. Bispyribac-sodium presents a good eco-toxicology profile; it is suitable for application on paddy rice. Its chemical name is sodium 2,6-bis((4,6-dimethoxypyrimidin-2-yl)oxy)benzoate and has the following structure:



Imazethapyr belongs to the imidazolinone class of compounds and acts by inhibiting the Acetolactate Synthase (ALS) enzyme. This leads to disruption of the DNA synthesis and cell growth. It is a broad spectrum herbicide which controls broad leaved weeds as well as grasses. It is taken up by the weeds through roots and leaves. Imazethapyr has excellent residual action making it a good candidate which can be used for resistance management.

Imazethapyr is an imidazolinone herbicide. Its chemical name is 2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-ethyl-3-pyridinecarboxylic acid. Its herbicidal activity is described in The Pesticide Manual, Fifteenth Edition, 2009. Imazethapyr controls many annual and perennial grass and broadleaf weeds in alfalfa, peas, beans, soybeans and imidazolinone tolerant rice and corn. Use as the acid or the ammonium salt is preferred with use as the ammonium salt being most preferred. As used herein, imazethapyr, which has the following structure:



Herbicidal combinations are used to control a broader range of weeds. However, the combination of herbicides may not always result in the desired effect. Sometimes a combination of herbicides may lead to an additive effect or an antagonistic effect instead of a synergistic effect. It may also result in phytotoxicity to the crops making it an undesirable combination. Therefore, there is a need to carefully select the herbicides at a specific ratio to offer a synergistic effect that achieves effective control of weeds while having no phytotoxic effect on the crop and reducing the chances of development of herbicide resistant weeds.

Therefore, there is a need in the art for combinations that have advantageous properties such as a herbicidal combination that is synergistic, reduces the dosage of herbicides used thus causing minimal damage to the environment, controlling a broader range of weeds, having no phytotoxic effect on the crop, helps in resistance management, along with that has excellent residual effects. A variety of chemicals and chemical formulations effective in the control of unwanted vegetation have been synthesized and evaluated. However, there remains a need for improved compositions and methods of use thereof that are effective in controlling undesirable vegetation.

OBJECTIVE OF THE INVENTION:

The main objective of the present invention is to provide a herbicidal combination comprising a) a pyrimidinyl benzoate derivative; and b) an imidazolinone derivative.

Another objective of the present invention is to provide a herbicidal combination comprising a) a pyrimidinyl benzoate derivative selected from bispyribac, bispyribac-sodium, pyribenzoxim, pyriftalid, or pyriminobac-methyl; and b) an imidazolinone derivative selected from imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin or imazethapyr.

Another objective of the present invention is to provide a herbicidal combination comprising a) bispyribac or agrochemically acceptable salt(s) thereof; and b) an imidazolinone derivative selected from imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin or imazethapyr.

Another objective of the present invention is to provide a synergistic herbicidal combination comprising a) bispyribac or bispyribac-sodium; and b) imazethapyr or agrochemically acceptable salt(s) thereof.

Yet another objective of the present invention is to provide a method of controlling weeds which comprises contacting the vegetation or the locus thereof with or applying an herbicidal combination of the present invention to the soil or water to prevent the emergence or growth of vegetation.

Yet another objective of the present invention is to provide a herbicidal composition comprising a synergistic herbicidal combination.

Yet another objective of the present invention is to provide a synergistic herbicidal combination which offers a broader and more complete spectrum of weed control.

Yet another objective of the present invention is to provide a synergistic herbicidal combination which provides a better control of weeds at lower use rates, and which gives good residual control.

Yet another objective of the present invention is to provide a herbicidal combination which is synergistic and thus helps in resistance management.

Yet another object of the present invention is to provide a method of improving the plant health or increasing yield in a crop by the application of a synergistic herbicidal combination.

Some or all these and other objects of the invention can be achieved by way of the invention described hereinafter.

SUMMARY OF THE INVENTION:

Accordingly, the present invention provides a herbicidal combination comprising:

a) a pyrimidinyl benzoate derivative; and
b) an imidazolinone derivative.

The pyrimidinyl benzoate derivative which can be used in the present invention is selected from bispyribac, bispyribac-sodium, pyribenzoxim, pyriftalid, or pyriminobac-methyl.

The imidazolinone derivative which can be used in the present invention is selected from imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin or imazethapyr.

In one embodiment, the present invention provides a herbicidal combination comprising:

a) bispyribac or agrochemically acceptable salt(s) thereof; and
b) an imidazolinone derivative selected from imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin or imazethapyr.

In another embodiment, the present invention provides a herbicidal combination comprising:

a) bispyribac or agrochemically acceptable salt(s) thereof; and
b) imazethapyr or agrochemically acceptable salt(s) thereof.

In still another embodiment, the present invention provides a herbicidal composition comprising:

a) bispyribac or agrochemically acceptable salt(s) thereof;
b) imazethapyr or agrochemically acceptable salt(s) thereof; and
c) at least one agrochemically acceptable excipient(s).

In still another embodiment, the present invention provides a method of controlling weeds at a locus, said method comprising applying a herbicidal composition comprising:

a) bispyribac or agrochemically acceptable salt(s);
b) imazethapyr or agrochemically acceptable salt(s); and
c) at least one agrochemically acceptable excipient(s).

The weight ratio of herbicide (a) to herbicide (b) is in the range from 1:100 to 100:1; preferably from 1:80 to 80:1, more preferably 1:10 to 10:1, and most preferably 1:4 to 4:1.

In one embodiment, the present invention provides a herbicidal combination or composition may further comprise at least one insecticide(s), fungicide(s), acaricide(s), nematicide(s), herbicide(s), safener(s), plant growth regulator(s), biostimulant(s) and combination thereof.

In yet another embodiment, the present invention provides a method for controlling undesirable vegetation or weeds at a locus, wherein, the method comprising applying to the locus, a herbicidal combination comprising:

a) bispyribac or agrochemically acceptable salt(s) thereof; and
b) imazethapyr or agrochemically acceptable salt(s) thereof.

DETAILED DESCRIPTION OF THE INVENTION:

ABBREVIATIONS

AE: Aerosol	SG: Water soluble granule
CS: Capsule suspension	SP: Water soluble powder
DP: Dustable powder	SU: Suspension
EC: Emulsifiable concentrate	ME: Micro-emulsion
EG: Emulsifiable granule	OD: Oil dispersion
EW: Oil-in water emulsion	ULV: Ultra-low volume liquid
e.g.: Example	WG/WDG: Water dispersible granule
GR: Granule	WP: Wettable powder
SC: Suspension concentrate	WT: Water dispersible tablet
TB: Tablet	UL: Liquid
SP: Water soluble powder	EG: Emulsifiable granule
EO: Emulsion oil in water	ES: Emulsion for seed treatment
OF: Oil miscible flowable concentrate	OP: Oil dispersible powder
CS: capsule suspension	SG: Water soluble granule
LS: Solution for seed treatment	FS: Flowable concentrate for seed treatment
SE: Suspo-emulsion	ZC: mixed formulation of CS and SC
ZE: mixed formulation of CS and SE	ZW: mixed formulation of CS and EW

DEFINITIONS

The foregoing definitions provided herein for the terminologies used in the present disclosure are for illustrative purpose only and in no manner limit, the scope of the present invention disclosed in the present disclosure.

It will be understood that the terminology used herein is for the purpose of describing embodiments only, and is not intended to be limiting. As used in this specification, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, the reference to "a surfactant" includes one or more of such surfactants.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one ordinary skilled in the art to which the invention pertains. Although other methods and materials similar, or equivalent, to those described herein can be used in the practice of the present invention, the preferred materials and methods are described herein.

As used herein, the terms "comprises", "comprising", "includes", "including", or any other variation thereof, are intended to cover a non-exclusive inclusion, subject to any limitation explicitly indicated. For example, a composition or a method that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, or method.

As used herein, the term "agrochemically acceptable salts" are typically acid addition salts of inorganic or organic acids, preferably of hydrochloric acid, hydrobromic acid, sulfuric acid, nitric acid, perchloric acid, phosphoric acid, formic acid, acetic acid, trifluoroacetic acid, oxalic acid, malonic acid, toluenesulfonic acid or benzoic acid.

As used herein, the term "bispyribac or agrochemically acceptable salts" is a salt of bispyribac e.g. bispyribac-sodium.

As used herein, the term “composition” or "formulation" can be used interchangeably, unless stated otherwise, is meant to encompass, and are not limited to, compositions or formulations containing the combination of bispyribac or bispyribac-sodium and imazethapyr.

As used herein, the term “additive(s)” or "auxiliary agent(s)" or “agriculturally acceptable carrier(s)” can be used interchangeably and refers to inert substances which are commonly used as diluent, to provide stability or to increase the activity profile of the composition or formulation with or without having agrochemical activity.

As used herein, the term “surfactant(s)” means a compound that, when dissolved in a liquid, reduces the surface tension of the liquid, which reduces the interfacial tension between two liquids or which reduces surface tension between a liquid and a solid.

As used herein, the term “stabilizer(s)” refers to a substance capable of imparting resistance against physical or chemical deterioration or deformulation.

As used herein, the term “defoaming agent(s)” refers to a chemical additive that reduces and hinders the formation of foam in the industrial process liquids, semi-solids, or solids. The terms defoaming agent and anti-foaming agent can be used interchangeably.

As used herein, the term “thickener(s)” refers to a polymeric material, which at a low concentration increases the viscosity of an aqueous solution and helps to stabilize the composition.

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

As used herein, the term “herbicide” shall mean an active ingredient that kills, controls or otherwise adversely modifies the growth of plants. As used herein, a herbicidally effective or vegetation controlling amount is an amount of active ingredient that causes a "herbicidal effect," i.e., an adversely modifying effect and includes deviations from natural development, killing, regulation, desiccation, retardation. The terms "plants" and "vegetation" include, but are not limited to, germinant seeds, emerging seedlings, plants emerging from vegetative propagules, and established vegetation.

As used herein, the term “plant parts” are understood to mean all above-ground and below-ground parts and organs of plants, such as shoot, leaf, flower and root, examples including leaves, needles, stems, stalks, flowers, fruit-bodies, fruits and seeds, and also roots, tubers and rhizomes. The plant parts also include harvested plants and vegetative and generative propagation material, for example seedlings, tubers, rhizomes, cuttings and seeds.

As used herein, the term “locus" means a plant, plant parts, plant propagation material (preferably seed), soil, area, material or environment in which a pest is growing or may grow. Also, denote the vicinity of a desired crop in which weed control, typically selective weed control is desired. The locus includes the vicinity of desired crop plants wherein the weed infestation has either emerged or is yet to emerge. The term crop shall include a multitude of desired crop plants or an individual crop plant growing at a locus.

As used herein, the term “polymorph” encompasses the different crystal forms of compound. When a compound recrystallizes from a solution or slurry, it may crystallize with different spatial lattice arrangements, a property referred to as “polymorphism”. Different polymorphic forms of a given substance may differ from each other with respect to one or more physical properties, such as solubility and dissociation, true density, crystal shape, compaction behavior, flow properties, and/or solid state stability.

As used herein, the term "effective amount" means the amount of the active substances in the compositions to achieve an observable effect on growth, including the effects of necrosis, death, retardation, prevention, and removal, destruction, or otherwise diminishing the occurrence and activity of the target organism. The effective amount can vary for the various compositions used in the present invention. An effective amount of the compositions will also vary according to the prevailing conditions such as desired pesticidal effect and duration, weather, target species, locus, mode of application, and the like.

As used herein, the term “agriculturally acceptable additives” means it contains additional additives selected from: solid carrier(s), liquid carrier(s), gaseous carrier(s), surfactant(s), binder(s), disintegrating agent(s), antioxidant(s), osmotic agent(s), wetting agent(s), pH adjuster(s), thickener(s), preservative(s), filler(s), diluent(s), emulsifier(s), anti-caking agent(s), anti-freezing agent(s),

defoaming agent(s), viscosifying agent(s), extender(s), buffering agent(s), solubilizer(s), chelating agent(s), stabilizer(s) and/or coloring agent(s) or combination thereof.

In one embodiment, the present invention provides a herbicidal combination comprising:

a) a pyrimidinyl benzoate derivative; and
b) an imidazolinone derivative.

The pyrimidinyl benzoate derivative which can be used in the present invention is selected from bispyribac, bispyribac-sodium, pyribenzoxim, pyriftalid, or pyriminobac-methyl.

The imidazolinone derivative which can be used in the present invention is selected from imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin or imazethapyr.

In another embodiment, the present invention provides a herbicidal combination comprising:

a) bispyribac or agrochemically acceptable salt(s) thereof; and
b) an imidazolinone derivative selected from imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin or imazethapyr.

In yet another embodiment, the present invention provides the herbicidal combinations comprising a) a pyrimidinyl benzoate derivative selected from the group consisting of bispyribac, bispyribac-sodium, pyribenzoxim, pyriftalid, or pyriminobac-methyl; b) an imidazolinone derivative selected from the group consisting of imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin or imazethapyr; are present in most preferred combinations as below:

Sr. No.	**Herbicide a) a pyrimidinyl benzoate derivative**	**Herbicide b) an imidazolinone derivative**
1	bispyribac	imazamethabenz
2	bispyribac	imazamethabenz-methyl
3	bispyribac	imazamox
4	bispyribac	imazapic
5	bispyribac	imazapyr
6	bispyribac	imazaquin
7	bispyribac	imazethapyr
8	bispyribac-sodium	imazamethabenz
9	bispyribac-sodium	imazamethabenz-methyl
10	bispyribac-sodium	imazamox
11	bispyribac-sodium	imazapic
12	bispyribac-sodium	imazapyr
13	bispyribac-sodium	imazaquin
14	bispyribac-sodium	imazethapyr
15	pyribenzoxim	imazamethabenz
16	pyribenzoxim	imazamethabenz-methyl

17	pyribenzoxim	imazamox
18	pyribenzoxim	imazapic
19	pyribenzoxim	imazapyr
20	pyribenzoxim	imazaquin
21	pyribenzoxim	imazethapyr
22	pyriftalid	imazamethabenz
23	pyriftalid	imazamethabenz-methyl
24	pyriftalid	imazamox
25	pyriftalid	imazapic
26	pyriftalid	imazapyr
27	pyriftalid	imazaquin
28	pyriftalid	imazethapyr
29	pyriminobac-methyl	imazamethabenz
30	pyriminobac-methyl	imazamethabenz-methyl
31	pyriminobac-methyl	imazamox
32	pyriminobac-methyl	imazapic
33	pyriminobac-methyl	imazapyr
34	pyriminobac-methyl	imazaquin
35	pyriminobac-methyl	imazethapyr

In another embodiment, the present invention provides a herbicidal combination comprising:

a) bispyribac or agrochemically acceptable salt(s) thereof; and

b) imazethapyr or agrochemically acceptable salt(s) thereof.

In yet another embodiment, the present invention provides a herbicidal combination comprising:

a) bispyribac or bispyribac-sodium; and

b) imazethapyr or agrochemically acceptable salt(s) thereof.

The inventors have surprisingly found that bispyribac or agrochemically acceptable salt(s) thereof, when combined with imazethapyr or agrochemically acceptable salt(s) thereof has resulted in an unexpected synergy. Without wishing to be bound by theory, it was found that bispyribac or bispyribac-sodium, even when added in minute quantities, surprisingly increased the efficacy of the imazethapyr, causing a synergistic reaction.

The weight ratio of herbicide (a) to herbicide (b) is in the range from 1:100 to 100:1; preferably from 1:80 to 80:1, more preferably 1:10 to 10:1, and most preferably 1:4 to 4:1

In one embodiment, the weight ratio of herbicide (a) to herbicide (b) ranges from 1:3 to 3:1, 1:2 to 2:1, or 1:1.

In another embodiment, the present invention provides a herbicidal composition comprising:

a) a pyrimidinyl benzoate derivative;

b) an imidazolinone derivative; and

c) at least one agrochemically acceptable excipient(s).

In another embodiment, the present invention provides a herbicidal composition comprising:

a) bispyribac or agrochemically acceptable salt(s) thereof;

b) an imidazolinone derivative selected from imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin or imazethapyr; and

c) at least one agrochemically acceptable excipient(s).

In another embodiment, the present invention provides a herbicidal composition comprising:

a) bispyribac or agrochemically acceptable salt(s);

b) imazethapyr or agrochemically acceptable salt(s); and

c) at least one agrochemically acceptable excipient(s).

In yet another embodiment, the present invention provides a herbicidal composition comprising:

a) bispyribac or bispyribac-sodium;

b) imazethapyr or agrochemically acceptable salt(s) thereof; and

c) at least one agrochemically acceptable excipient(s).

The total amount of herbicide (a) in the composition may typically be in the range of 0.1 to 99% by weight, preferably 0.2 to 90% by weight, more preferably 1 to 80% by weight. The total amount of the herbicide (b) in the composition may be in the range of 0.1 to 99% by weight, preferably 0.2 to 90% by weight, preferably 1 to 80% by weight.

The active ingredient imazethapyr used may in the crystalline form 1 and/or form 2, and can be obtained by following the process disclosed in patent e.g. CN111233828.

The present invention provides a combination/ composition of bispyribac or bispyribac-sodium and imazethapyr, wherein the active ingredients bispyribac or bispyribac-sodium and imazethapyr have a particle size of 1 to 80 µm, more preferably 1 to 30 µm, most preferably 1 to 10 µm.

In yet another embodiment, the present invention may be a composition is formulated as a dusts, a microcapsule, a solution, a suspension concentrate (SC), a water dispersible granule (WDG)/(WG), a tablet (TB), a wettable powder (WP), a water dispersible tablet (WT), an ultra-low volume (ULV) liquid (UL), a suspension (SU), a water soluble powder (SP), a suspo-emulsion (SE), a granule (GR), an oil-in-water emulsion (EW), an emulsifiable granule (EG), an emulsion oil in water (EO), an emulsifiable powder (EP), an emulsion for seed treatment (ES), a solution for seed treatment (LS), a flowable concentrate for seed treatment (FS), an emulsifiable concentrate (EC), a micro-emulsion (ME), an oil-in-water emulsions (EW), an oil miscible flowable concentrate (oil miscible suspension) (OF), an oil dispersible powder (OP), an oil dispersion (OD), a capsule suspension (CS), a dustable powder (DP), a

soluble concentrate (SL), a water soluble granule (SG), an aerosol (AE), a mixed formulation of CS and SL, a mixed formulation of CS and SC (ZC), a mixed formulation of CS and SE (ZE), or a mixed formulation of CS and EW (ZW).

In one embodiment, the present invention provides a process for the preparation of a composition of a pyrimidinyl benzoate derivative and an imidazolinone derivative, comprising the steps of:

a) adding a pyrimidinyl benzoate derivative and an imidazolinone derivative and optionally, at least one additional active selected from insecticide(s), acaricide(s), nematicide(s), fungicide(s), herbicide(s), safener(s), plant growth regulator(s) or mixtures thereof;
b) adding agrochemically acceptable excipient(s) uniformly in a mixer; and optionally milling by a mill.

In a preferred embodiment, the present invention provides water dispersible granule (WDG/WG) composition of bispyribac or bispyribac-sodium and imazethapyr.

In another embodiment, the present invention provides a process of preparing of a water dispersible granule (WDG/WG) formulation comprising the steps of:

a) mixing active ingredients, dispersing agent, wetting agent, disintegrating agent, defoamer and filler in a blender to form a homogenous mass;
b) milling the homogenous mass to obtain particle size below 10 microns;
c) preparing a dough using the above milled material by using 10 to 20% water;
d) extruding the dough using a extruder having a suitable screen by maintaining the temperature of the screen below 50°C to obtain extruded granules;
e) drying the extruded granules using a fluid bed dryer by keeping air flow at 75% to 80% and maintaining the temperature of the air at 50°C to obtain free flowing WDG/WG formulation.

In a preferred embodiment, the present invention provides a suspension concentrate (SC) composition of bispyribac or bispyribac-sodium and imazethapyr.

In a preferred embodiment, the present invention provides a wettable powder (WP) composition of bispyribac or bispyribac-sodium and imazethapyr.

In a preferred embodiment, the present invention provides water dispersible granule (WDG/WG) composition of bispyribac or bispyribac-sodium and imazamox.

In a preferred embodiment, the present invention provides a suspension concentrate (SC) composition of bispyribac or bispyribac-sodium and imazamox.

In a preferred embodiment, the present invention provides a wettable powder (WP) composition of bispyribac or bispyribac-sodium and imazamox.

In a preferred embodiment, the present invention provides water dispersible granule (WDG/WG) composition of bispyribac or bispyribac-sodium and imazamethabenz-methyl.

In a preferred embodiment, the present invention provides a suspension concentrate (SC) composition of bispyribac or bispyribac-sodium and imazamethabenz-methyl.

In a preferred embodiment, the present invention provides a wettable powder (WP) composition of bispyribac or bispyribac-sodium and imazamethabenz-methyl.

In a preferred embodiment, the present invention provides water dispersible granule (WDG/WG) composition of bispyribac or bispyribac-sodium and imazaquin.

In a preferred embodiment, the present invention provides a suspension concentrate (SC) composition of bispyribac or bispyribac-sodium and imazaquin.

In a preferred embodiment, the present invention provides a wettable powder (WP) composition of bispyribac or bispyribac-sodium and imazaquin.

In a preferred embodiment, the present invention provides water dispersible granule (WDG/WG) composition of pyriminobac-methyl and imazaquin.

In a preferred embodiment, the present invention provides a suspension concentrate (SC) composition of pyribenzoxim and imazamethabenz-methyl.

In a preferred embodiment, the present invention provides a wettable powder (WP) composition of pyribenzoxim and imazamox.

In one embodiment, the present invention provides a composition of bispyribac or bispyribac-sodium and imazethapyr comprising organic or inorganic carrier material, including agriculturally acceptable additive(s) selected from the group comprising of solid carrier(s), liquid carrier(s), gaseous carrier(s), surfactant(s), binder(s), disintegrating agent(s), antioxidant(s), osmotic agent(s), wetting agent(s), pH adjuster(s), thickener(s), preservative(s), filler(s), diluent(s), emulsifier(s), anti-caking agent(s), anti-freezing agent(s), defoaming agent(s), viscosifying agent(s), extender(s), buffering agent(s), solubilizer(s), chelating agent(s), stabilizer(s) and/or coloring agent(s) or combination thereof. The composition may also contain if desired, one or more auxiliaries customary for crop protection compositions.

Solid carriers are selected from the group comprising of, but are not limited to, pyrophyllite clay, silica, precipitated silica, kaolin clay, kieselguhr, chalk, diatomaceous earth, lime, calcium carbonate, bentonite clay, Fuller's earth, talc, cottonseed hulls, wheat flour, soybean flour, pumice, wood flour, attapulgite, walnut shell flour, lignin, cellulose etc. These solid carriers may be used alone or in combination thereof. On the other hand, solid carriers may act as structurants.

Liquid carrier(s) is selected from the group comprising of, but not limited to, water; alcohols such as ethanol, propanol, butanol, n-octanol, isopropanol ethylene glycol, diethylene glycol, propylene glycol, polyethylene glycol, benzyl alcohol, glycerin; polyol ethers such as ethylene glycol monopropyl ether, diethylene glycol monomethyl ether, dipropylene glycol dimethyl ether; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone; ethers such as dipropyl ether, dioxane, tetrahydrofuran, aliphatic hydrocarbons such as normal paraffin, isoparaffin, kerosene, mineral oil; aromatic hydrocarbons such as xylene, toluene, naphthene, solvent naphtha, solvent C9, solvent C10, solvent C12, solvesso 100, solvesso 150, solvesso 200; chlorinated aliphatic or aromatics hydrocarbons such as chlorobenzene, chloroethylene, methylene chloride; esters such as ethyl acetate, diisopropyl phthalate, dimethyl adipate, methyl oleate, methyl tallowate; lactones such as gamma-butyrolactone, gamma-valerolactone, epsilon-caprolactone; amides such as dimethylformamide, N-methylpyrrolidone, N-octylpyrolidone, N,N-dimethyldecanamide; nitriles such as acetonitrile; organosulfur compound such as dimethyl sulfoxide; vegetable oils such as soybean oil, rapeseed oil, cotton seed oil. These liquid carriers may be used alone or in combination.

Gaseous carrier(s) is selected from the group comprising of, but not limited to, liquefied petroleum gas, air, nitrogen, carbon dioxide or dimethyl ether. These gaseous carriers may be used alone or in combination thereof.

Surfactant(s) are nonionic or anionic surfactants or a combination of these surfactants. It is preferred to use one or more than one kind of surfactant. Surfactant(s) is selected from the group comprising of, but not limited to, sugar esters such as sorbitan monolaurate, polyoxyethylene sorbitan monolaurate; sodium alkylethersulfate, sodium lauryl sulfate, sodium dodecyl sulfate; C_1-C_{30} alkylcarboxylate, C_1-C_{20} hydroxyalkylcarboxylate, polymer containing carboxylate, arylcarboxylate, alkylx (e.g. aliphatic di- and tricarboxylates) having 2 to 32 carbon atoms, such as aconitic acid, adipic acid, aspartic acid, citric acid, fumaric acid, galactaric acid, glutamic acid, glutaric acid, oxoglutaric acid, maleic acid, malic acid, malonic acid, oxalate, sebacic acid, succinic acid, tartaric acid; alkyl polyglucoside such as decyl glucoside; polyoxyethylene alkyl ethers such as polyoxyethylene lauryl ether, or polyoxyethylene coconut fatty alcohol ether; polyoxyethylene alkynyl ether such as polyoxyethylene 2,4,7,9-tetramethyl-5-decyn-4,7-diol ether; polyoxyethylene aryl ethers such as polyoxyethylene nonylphenyl ether or polyoxyethylene tristyrylphenyl ether; polyoxyethylene vegetable oil ethers such as polyoxyethylene castor oil or polyoxyethylene hydrogenated castor oil; vegetable oil ethoxylate; C_6-C_{20} linear and branched alcohol ethoxylates, C_6-C_{20} alcohol propoxylates, C_6-C_{20} propoxylated and ethoxylated alcohols; polyoxyethylene fatty acid esters such as polyoxyethylene monolaurate, polyoxyethylene distearate or polyoxyethylene resin acid ester; polyoxyethylene polyoxypropylene (EO-PO) block copolymers such as Pluronic®; polyoxyethylene polyoxypropylene alkyl ether such as polyoxyethylene polyoxypropylene lauryl ether; polyoxyethylene polyoxypropylene aryl ether such as polyoxyethylene polyoxypropylene styrylphenyl ether; a modified styrene acrylic polymer,

polyoxyethylene alkyl amines such as polyoxyethylene stearyl amine; polyoxyethylene fatty acid amide such as lauric acid diethanolamid; fluorinated surfactant; alkyl sulfates such as sodium lauryl sulfate; sodium alkylbenzene sulfonate, calcium alkylbenzene sulphonate; polyoxyethylene alkyl ether sulfates such as sodium polyoxyethylene lauryl ether sulfate; polyoxyethylene aryl ether sulfates such as sodium polyoxyethylene nonylphenyl ether sulfate or ammonium polyoxyethylene tristyrylphenyl ether sulfate; aryl sulfonate such as calcium benzene sulfonate calcium dodecyl benzene sulfonate, sodium naphthalene sulfonate, sodium salt of naphthalene sulfonate condensate (MORWET® D-425) or sodium naphthalene sulfonate formaldehyde condensate; poly aryl phenyl ether sulphate ammonium salt; 'alpha'-olefin sulfonate; lauryl sulfosuccinate, laureth sulfosuccinate, laureth-5 sulfosuccinate, ricinoleamide MEA sulfosuccinate, undecylenearnide MEA sulfosuccinate, diisobutyl sulfosuccinate, dioctyl sulfosuccinate, dihexyl sulfosuccinate, dicyclohexyl sulfosuccinate, diisodecyl sulfosuccinate, diisotridecyl sulfosuccinate, di-2-ethylhexyl sulfosuccinate, di-2-methylamyl sulfosuccinate, dimethylamyl sulfosuccinate, dibutylhexyl sulfosuccinate, diisooctyl sulfosuccinate or their alkali metal salts, sodium lignosulfonate; polycarboxylic acid sodium salt; N-methyl fatty acid sarcosinate; polyoxyethylene alkyl ether phosphate; polyoxyethylene aryl ether phosphates such as polyoxyethylene phenyl ether phosphate; polyoxyethylene alkyl phenyl ether phosphate; graft co-polymers such as polymethyl methacrylate-polyethylene glycol graft copolymer. These surfactants may be used alone or in combination thereof.

Suitable stabilizing surfactants include anionic, cationic, nonionic and amphoteric surfactants, block polymers and polyelectrolytes. Further on, polysaccharide (e.g. starch, starch derivatives, cellulose derivatives, xanthan gum, and gelatin) may be used as stabilizing surfactants. Preferred stabilizing surfactants are nonionic surfactants (preferably alkoxylates, such as comb polymers) and/or block polymers, and EO-PO block copolymers. Mixtures of aforementioned stabilizing surfactants are also suitable. On the other hand, surfactants may act as detergents, wetting agents, emulsifiers, foaming agents, dispersants/dispersing agents, spreader, adjuvant for penetration enhancement, rain fastness, or soil leaching control etc.

Wetting agent(s) is selected from the group comprising of, but not limited to, one or more of dioctyl sulfosuccinate, poly oxy alkylene alkyl ether, poly oxy alkylene alkyl phenyl ether sulfonates, dialkylsuccinate, Sodium blend of alkyl naphthalene sulfonate, sodium dioctyl sulphosuccinate & sodium lauryl sulfonate preferably sodium lauryl sulfate, blend of alkyl naphthalene sulfonate etc.

The dispersing agent(s) is selected from the group comprising of, but not limited to, one or more of poly carboxylates, alkyl naphthalene sulfonates, phenol sulphonic acid condensates, ligno sulphonates, methyl oleyl taurates, sodium lignosulfonate, polymethyl methacrylate-polyethylene glycol graft copolymer (Atlox 4913), polyoxyethylene alkyl ether (Atlox 4894), Ufoxane 3A, silica poly ether copolymer and poly vinyl alcohols, sodium salt of naphthalene sulfonate condensate, atlox metaspese 5505, mixture of salt of naphthalene sulphonic acid and phenol sulphonic acid condensate, Sulfonated

aromatic polymer, Sodium salt preferably sodium salt of naphthalene sulfonate condensate, castor oil ethoxylate.Penetrant(s) is selected from the group comprising of, but not limited to, one or more of alcohol, glycol, glycol ether, ester, amine, alkanolamine, amine oxide, quaternary ammonium compound, triglyceride, fatty acid ester, fatty acid ether, N-methyl pyrrolidone, dimethylformamide, dimethyl acetamide, dimethyl sulfoxide, polyoxyethylenetrimethylolpropanemonooleate, polyoxyethylenetrimethylolpropanedioleate, polyoxyethylenetrimethylolpropanetrioleate, polyoxyethylenesorbitanmonooleate, polyoxyethylene sorbitol hexaoleate and methylated soybean oil. However, those skilled in the art will appreciate that it is possible to utilize different penetrants without departing from the scope of the present invention.

Solvent(s) is selected from the group comprising of, but not limited to, one or more of C2-C4-alkyl lactates, in particular from glycerin triacetate, ethyl lactate, n-propyl lactate and isopropyl lactate. In one embodiment solvent is selected from C6-C10-alkyl lactates, such as n-hexyl lactate, 1-ethylhexyl lactate, 1-methylhepytyl lactate, 1,3-dimethylhexyl lactate, 2-methylheptyl lactate, 2,4-dimethylhexyllactate, 2,2,4-trimethylpentyl lactate, n-octyl lactate, 2-ethylhexyl lactate, n-nonyl lactate, 1-methyloctyl lactate, 2-methyloctyl lactate, 1-methylnonyl lactate, 2-propylheptyl lactate and n-decyl lactate, 2,2,4- trimethylpentyl lactate, butyl lactate, isopropyl myristate, hexylene glycol, dioxane, d-limonene, a C_1-C_{14} saturated straight-chain alcohol, isopropyl alcohol, 2-butanol, isobutyl alcohol, tertiary butyl alcohol, 2-butoxyethanol, 2-phenylethanol, diacetone alcohol, γ-butyrolactone, nitromethane, acetophenone, triacetin, pyridine, water, toluene, xylene, petroleum naphtha, crop oil, acetone, methyl ethyl ketone, cyclohexanone, acetic anhydride, acetonitrile, acetophenone, amyl acetate, 2-butanone, chlorobenzene, cyclohexane, cyclohexanol, alkyl acetates, diacetonalcohol, 1 ,2-dichloropropane, diethanolamine, p- diethylbenzene, abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, *N,N*-dimethyl formamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkyl pyrrolidinone, ethyl acetate, 2-ethyl hexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha pinene, d-limonene, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol diacetate, glycerol monoacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropyl benzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxy-propanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, n-hexane, n-octylamine, octadecanoic acid, octyl amine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol (PEG400), propionic acid, propylene glycol, propylene glycol monomethyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylene sulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, methanol, ethanol, isopropanol, and higher molecular weight alcohols such as amyl

alcohol, tetrahydrofurfuryl alcohol, hexanol, octanol, etc. ethylene glycol, propylene glycol, glycerine, *N*-methyl-2- pyrrolidinone, and the like.

A green solvent is a solvent which is naturally occurring and which has been found not harm the environment when used on an industrial scale. In one embodiment, the green solvent slected from but mot limited to water, glycerin triacetate, ethyl lactate or an alcohol based solvent (e.g., ethanol).

In another embodiment, solvent(s) is selected from the group comprising of, but not limited to, one or more of glycerin triacetate and ethyl lactate.

Oil(s) is selected from the group comprising of, but not limited to, a light paraffin oil, plant oil, mineral oil, petroleum oil, vegetable oil or animal oil or derivatives or mixtures thereof. However, those skilled in the art will appreciate that it is possible to utilize other water immiscible solvents without departing from the scope of the present invention.

The mineral oil or petroleum oil can be one or more of aliphatic or isoparaffinic series, and mixtures of aromatic and aliphatic hydrocarbons; halogenated aromatic or aliphatic hydrocarbons. Paraffinic oil can be selected from linear or branched C8 to C30 paraffins for example such as octane, nonane, decane, undecane, dodecane, tridecane, tetradecane, pentadecane, hexadecane, their mixtures, or mixtures thereof with higher boiling homologs, such as hepta-, octa-, nonadecane, eicosane, heneicosane, docosane, tricosane, tetracosane, pentacosane, and the branched chain isomers thereof, unsubstituted or substitutedaromatic or cycloaliphatic C7 to C18 hydrocarbon compounds such as mono- or polyalkylsubstituted benzenes, or mono- or polyalkyl-substituted naphthalenes, or transesterification products thereof, liquid esters of C1 to C12 alcohols such as butanol, n-octanol, i-octanol, dodecanoi, cyclopentanol, cyclohexanol, cyclooctanol, ethylene glycol or propylene glycol with C2 to C12 carboxylic or polycarboxylic acids, such as caproic acid, capric acid, caprylic acid, pelargonic acid, succinic acid and glutaric acid; or with aromatic carboxylic acids such as benzoic acid, toluic acid, salicylic acid and phthalic acid, liquid amides of Cl to C5 amines, alkylamines or alkanolamines with C6 to Cl8 carboxylic acids, or derivatives thereof. Esters which can be used in the oil dispersions of the invention are benzyl acetate, caproic acid ethyl ester, pelargonic acid ethyl ester, benzoic acid methyl or ethyl ester, salicylic acid methyl, propyl, or butyl ester, diesters of phthalic acid with saturated aliphatic or alicyclic C_1 to C_{12} alcohols, such as phthalic acid dimethyl ester, dibutyl ester, diisooctyt ester, or liquid amides of C_1-C_3 amines, alkylamines or alkanolamines with C_6 – C_{18} carboxylic acids or derivatives or mixtures thereof. However, those skilled in the art will appreciate that it is possible to utilize other mineral or pertroleum oils without departing from the scope of the present invention.

The vegetable oils can be one or more of seed oil. The vegetable oils can also include one or more of soy bean oil, methylated soybean oil, rape seed oil, olive oil, castor oil, sunflower seed oil, coconut oil, com oil, cotton seed oil, linseed oil, palm oil, peanut oil, safflower oil, sesame oil, kapok oil, papaya oil, camellia oil, rice bran oil, tung oil and the like; and esters of the above vegetable oils, or

transesterification products thereof such as soy bean oilmethyl esters, ethyl esters, propyl esters, butyl esters or derivatives thereof. The animal oil can be one or more of whale oil, cod-liver oil, or mink oil. However, those skilled in the art will appreciate that it is possible to utilize other vegetable or animal oils without departing from the scope of the present invention.

Filler(s) is selected from the group comprising of, but not limited to, bentonite, perlite, talc, kaolin, sodium sulphate, sodium sulfate, aluminium silicate, diatomaceous earth, attapulgite, barium sulfate, mica, zeolites, calcium carbonate, fused sodium potassium, precipitated silica, precipitated silicates, aluminium silicate, sodium citrate, potassium citrate, magnesium citrate, and clay. These fillers may be used alone or in combination thereof.

Preservative(s)/biocide(s) is selected from the group comprising of, but not limited to, benzisothiazolinone (Proxel™ GXL), phenols, 2-bromo-2-nitropropane-1,3-diol (Bioban™ BP 30), 5-chloro-2-methyl-4-isothiazolin-3-one & 2 methyl-4-isothiazolin -3 one (Kathon™ CG/ICP), Glutaraldehyde (Ucarcide™ 50), Chloromethylisothiazolinone (CMIT)/Methylisothiazolinone (MIT) (Isocil® Ultra 1.5), 2.2-dibromo-3-nitrilopropioamide (Reputain™ 20), Natamycin & Nisin, Bronopol/CMIT/MIT (Mergal® 721K3). These Preservative(s)/biocide(s) may be used alone or in combination thereof.

Rheology modifier(s) selected from the group comprising of, but not limited to, water-soluble polymers such as polyvinyl alcohol and polyvinylpyrrolidone, polysaccharides such as arabic gum, alginic acid and the salt thereof, CMC (carboxymethyl-cellulose), xanthan gum, inorganic materials such as aluminum magnesium silicate and alumina sol. These rheology modifiers may be used alone or in combination thereof.

Stabilizer(s) is selected from the group comprising of, but not limited to, drying agent such as zeolite, quick lime or magnesium oxide; antioxidant agent such as phenol type, amine type, sulfur type or phosphorus type; or ultraviolet absorber such as salicylic acid type or a benzophenone type; or methylated soybean oil; or peroxide compounds such as hydrogen peroxide and organic peroxides, alkyl nitrites such as ethyl nitrite and alkyl glyoxylates such as ethyl glyoxylate, zeolite, antioxidants such as phenol compounds, phosphoric acid compounds and the like; ultraviolet absorbers such as benzophenone compounds or derivatives thereof. However, those skilled in the art will appreciate that it is possible to utilize other conventionally known stabilizers without departing from the scope of the present invention. These stabilizers may be used alone or in combination thereof.

In an embodiment, the present invention provides a process for the preparation of a composition comprising the steps of:

a) mixing bispyribac or agrochemically acceptable salt(s) thereof and imazethapyr or agrochemically acceptable salt(s) thereof,
b) adding agrochemically acceptable additives.

The formulation of the present invention can be applied by any one of the methods selected from atomization, spreading, dusting, spraying, diffusion, immersion, irrigation, injection, mixing, sprinkling (water immersion), foaming, dressing, coating, blasting, fumigation, smoking, smog and painting.

In an embodiment, the present invention provides a method of controlling weeds at a locus, the method comprising applying, to the locus, a combination comprising: a) bispyribac or agrochemically acceptable salt(s) thereof; and b) imazethapyr or agrochemically acceptable salt(s) thereof.

In another embodiment, the present invention provides a synergistic herbicidal combination comprising: a) bispyribac or agrochemically acceptable salt(s) thereof; and b) imazethapyr or agrochemically acceptable salt(s) thereof, which provides a better control of weeds at lower use rates, and which gives good residual control.

Yet another embodiment of the present invention provides a synergistic herbicidal combination comprising a) bispyribac or agrochemically acceptable salt(s) thereof; and b) imazethapyr or agrochemically acceptable salt(s) thereof, which offers a broader and more complete spectrum of weed control.

Yet another embodiment of the present invention provides a synergistic herbicidal combination comprising a) bispyribac or agrochemically acceptable salt(s) thereof; and b) imazethapyr or agrochemically acceptable salt(s) thereof, helps in resistance management.

Yet another embodiment of the present invention provides a method of improving the plant health or increasing yield in a crop by application of a synergistic herbicidal combination comprising a) bispyribac or agrochemically acceptable salt(s) thereof and b) imazethapyr or agrochemically acceptable salt(s) thereof.

Yet another embodiment of the present invention provides a method of controlling weeds at a locus, said method comprising applying a composition comprising a) bispyribac or agrochemically acceptable salt(s) thereof; b) imazethapyr or agrochemically acceptable salt(s) thereof, and (c) at least one agrochemically acceptable excipient.

Yet another embodiment the present invention provides a synergistic herbicidal composition comprising a) bispyribac or agrochemically acceptable salt(s) thereof; b) imazethapyr or agrochemically acceptable salt(s) thereof; and (c) at least one agrochemically acceptable excipient which provides a better control of weeds at lower use rates, and which gives good residual control.

Yet another embodiment of the present invention provides a synergistic herbicidal composition comprising a) bispyribac or agrochemically acceptable salt(s) thereof; b) imazethapyr or agrochemically acceptable salt(s) thereof; and (c) at least one agrochemically acceptable excipient which offers a broader and more complete spectrum of weed control.

Yet another embodiment of the present invention provides a synergistic herbicidal composition comprising a) bispyribac or agrochemically acceptable salt(s); b) imazethapyr or agrochemically acceptable salt(s); and (c) at least one agrochemically acceptable excipient helps in resistance management.

Yet another embodiment of the present invention provides a method of improving the plant health or increasing yield in a crop by application of a synergistic herbicidal composition comprising a) bispyribac or agrochemically acceptable salt(s); b) imazethapyr or agrochemically acceptable salt(s); and (c) at least one agrochemically acceptable excipient.

In an embodiment, the combination of the present invention may be combined with at least one other active ingredient selected from the group consisting of insecticide(s), fungicide(s), acaricide(s), nematicide(s), herbicide(s), safener(s), plant growth regulator(s), biostimulant(s) and combination thereof.

In one embodiment, the present invention provides a herbicidal combination comprising:

a) a pyrimidinyl benzoate derivative;
b) an imidazolinone derivative; and
c) at least one additional herbicide.

Thus, in an embodiment, the combination of the present invention may be combined with other additional herbicides. Exemplary herbicides that may be combined with the combination of the present invention may be selected from, but not limited to, herbicides belonging to classes such as ACCase inhibitors, ALS inhibitors, EPSP synthase inhibitors, synthetic auxins, auxin transport inhibitors, HPPD inhibitors, lipid synthesis inhibitors, long chain fatty acid inhibitors, as well as herbicides with unknown modes of action.

In an embodiment, the present invention may provide herbicidal combinations comprising bispyribac or bispyribac-sodium and imazethapyr or their salts or esters thereof and herbicidal safener.

In an embodiment, the safener may be selected from benoxacor, BPCMS, cloquintocet, cloquintocet-mexyl, mefenpyr-diethyl, cyometrinil, cyprosulfamide, dichlormid, dicyclonon, dietholate, fenchlorazole, fenchlorazole-ethyl, daimuron, cumyluron, dimepiperate, fenclorim, flurazole, fluxofenim, furilazole, isoxadifen, isoxadifen-ethyl, jiecaowan, jiecaoxi, mefenpyr, mephenate, metcamifen, naphthalic anhydride, oxabetrinil and their salts and esters. Additionally, it is believed that the use of safener composition with these herbicides may expand their usefulness on cereal crops.

In one embodiment, the present invention may be in a kit-of-parts comprising:

a) a first container comprising bispyribac or agrochemically acceptable salt(s) thereof;
b) a second container comprising imazethapyr or agrochemically acceptable salt(s) thereof; and
c) an instruction manual instructing the user to admix.

Each of the aspect described above may have one or more embodiments.

Each of the embodiments described hereinafter may apply to one or all of the aspects described hereinabove. These embodiments are intended to be read as being preferred features of one or all of the aspects described hereinabove. Each of the embodiments described hereinafter applies to each of the aspects described hereinabove individually.

In an embodiment, the present invention provides preferred combinations, compositions and methods thereof. The methods of the invention include a method of controlling weeds at a locus by applying to the locus the combination or the composition, or a method of increasing yield in a crop by application of the combination or composition, or a method of improving the plant health by application at the locus of the plant the combination or the composition. The embodiments described herein describe the preferred embodiments of all these possible combinations, compositions and methods of the invention.

The combination may be applied to the locus of the weeds in an herbicidally effective amount. The selection of the appropriate effective amounts depends on the density of weed infestation, weather patterns, crop health and many other factors, which may be made conveniently by a person skilled in the art. The effective amount of these herbicides in the synergistic combination of the present invention is not particularly limiting.

The herbicidal combination of the present invention maybe used to target weeds among the crops such corn, rice, wheat, barley, rye, oat, sorghum, cotton, soybean, common bean, hemp, peanut, buckwheat, beet, rapeseed, sunflower, sugar cane, tobacco, etc.; vegetables: solanaceous vegetables such as eggplant, tomato, pimento, pepper, potato, etc., cucurbit vegetables such as cucumber, pumpkin, zucchini, water melon, melon, squash, etc., cruciferous vegetables such as radish, white turnip, horseradish, kohlrabi, Chinese cabbage, cabbage, leaf mustard, broccoli, cauliflower, etc., asteraceous vegetables such as burdock, crown daisy, artichoke, lettuce, etc, liliaceous vegetables such as green onion, onion, garlic, and asparagus, ammiaceous vegetables such as carrot, parsley, celery, parsnip, etc., chenopodiaceous vegetables such as spinach, Swiss chard, etc., lamiaceous vegetables such as Perilla frutescens, mint, basil, etc, strawberry, sweet potato, Dioscorea japonica, colocasia, etc., flowers, foliage plants, turf grasses, fruits: pome fruits such apple, pear, quince, etc, stone fleshy fruits such as peach, plum, nectarine, Prunus mume, cherry fruit, apricot, prune, etc., citrus fruits such as orange, lemon, rime, grapefruit, etc., nuts such as chestnuts, walnuts, hazelnuts, almond, pistachio, cashew nuts, macadamia nuts, etc. berries such as blueberry, cranberry, blackberry, raspberry, etc., vines, kaki fruit, olive, plum, banana, oil palm, coffee, date palm, coconuts, etc., trees other than fruit trees; tea, mulberry, flowering plant, trees such as ash, birch, dogwood, Eucalyptus, Ginkgo biloba, lilac, maple, Quercus, poplar, Judas tree, Liquidambar formosana, plane tree, zelkova, Japanese arborvitae, fir wood, hemlock, juniper, Pinus, Picea, and Taxus cuspidate, etc.

Thus, in another aspect, the present invention provides a method of controlling weeds at a locus, the method comprising applying a combination comprising bispyribac or bispyribac-sodium and imazethapyr to the locus.

Thus, embodiments of the present invention may provide a method of controlling weeds at a locus, said method comprising application of synergistic combination of bispyribac or bispyribac-sodium and imazethapyr and optionally at least one insecticide(s), fungicide(s), acaricide(s), nematicide(s), herbicide(s), safener(s), plant growth regulator(s), biostimulant(s) and combination thereof.

In an embodiment, the present invention provides a method of controlling weeds at a locus for the burndown of weeds, said method comprising application at the locus of the weed a synergistic combination of bispyribac or bispyribac-sodium and imazethapyr.

The target weeds may be selected from Urticaceae weeds: *Urtica urens Polygonaceae weeds: Polygonum convolvulus, Polygonum lapathifolium, Polygonum pensylvanicum, Polygonum persicaria, Polygonum longisetum, Polygonum aviculare, Polygonum arenastrum, Polygonum cuspidatum, Rumex japonicus, Rumex crispus, Rumex obtusifolius, Rumex acetosa; Portulacaceae weeds: Portulaca oleracea; Caryophyllaceae weeds: Stellaria media, Cerastium holosteoides, Cerastium glomeratum, Spergula arvensis, Silene gallica Molluginaceae weeds: Mollugo verticillata; Chenopodiaceae weeds: Chenopodium album, Chenopodium ambrosioides, Kochia scoparia, Salsola kali, Atriplex spp.; Amaranthaceae weeds: Echinochloa colona, Echinochloa Crus-galli, Leptochloa chinensis, Cyperus iria Cyperus difformis, Fimbristylis Spp., Monochoria vaginalis, Eclipta alba, Ludwigia Spp., Sagittaria Spp.* and *Marsilea Spp.; Amaranthus retroflexus, Amaranthus viridis, Amaranthus lividus, Amaranthus spinosus, Amaranthus hybridus, Amaranthus palmeri, Amaranthus rudis, Amaranthus patulus, Amaranthus tuberculatos, Amaranthus blitoides, Amaranthus deflexus, Amaranthus quitensis, Alternanthera philoxeroides, Alternanthera sessilis, Alternanthera tenella; Papaveraceae weeds: Papaver rhoeas, Argemone Mexicana; Brassicaceae weeds: Raphanus raphanistrum, Raphanus sativus, Sinapis arvensis, Capsella bursa-pastoris, Brassica juncea, Brassica campestris, Descurainia pinnata, Rorippa islandica, Rorippa sylvestris, Thlaspi arvense, Myagrum rugosum, Lepidium virginicum, Coronopus didymus; Dinebra weeds: Dinebra Americana, Dinebra aquatic, Dinebra aristidoides, Dinebra bromoides, Dinebra calycina, Dinebra caudata, Dinebra chinensis, Dinebra chloride, Dinebra chondrosioides, Dinebra coerulescens, Dinebra cristata, Dinebra curtipendula, Dinebra decipiens, Dinebra divaricate, Dinebra divaricatissima, Dinebra dura, Dinebra guineensis, Dinebra hirsute, Dinebra hirta, Dinebra juncifolia, Dinebra ligulata, Dinebra lima, Dinebra melicoides, Dinebra nealleyi, Dinebra neesii, Dinebra panicea, Dinebra panicoides, Dinebra pubescens, Dinebra repens, Dinebra scabra, Dinebra secunda, Dinebra simoniana, Dinebra southwoodii, Dinebra squarrosa, Dinebra srilankensis, Dinebra tuaensis, Dinebra verticillate, Dinebra retroflexa. Dinebra haareri, Dinebra marquisensis, Dinebra perrieri, Dinebra polycarpha, Dinebra somalensis Capparaceae weeds: Cleome affinis; Fabaceae weeds: Aeschynomene indica,*

Aeschynomene rudis, Sesbania exaltata, Cassia obtusifolia, Cassia occidentalis, Desmodium tortuosum, Desmodium adscendens, Trifolium repens, Pueraria lobata, Vicia angustifolia, Indigofera hirsuta, Indigofera truxillensis, Vigna sinensis; Oxalidaceae weeds: Oxalis corniculata, Oxalis strica, Oxalis oxyptera; Geraniaceae weeds: Geranium carolinense, Erodium cicutarium; Euphorbiaceae weeds: Euphorbia helioscopia, Euphorbia maculate, Euphorbia humistrata, Euphorbia esula, Euphorbia heterophylla, Euphorbia brasiliensis, Acalypha australis, Croton glandulosus, Croton lobatus, Phyllanthus corcovadensis, Ricinus communis; Malvaceae weeds: Abutilon theophrasti, Sida rhombiforia, Sida cordifolia, Sida spinosa, Sida glaziovii, Sida santaremnensis, Hibiscus trionum, Anoda cristata, Malvastrum coromandelianum Sterculiaceae weeds: Waltheria indica; Violaceae weeds: Viola arvensis, Viola tricolor; Cucurbitaceae weeds: Sicyos angulatus, Echinocystis lobata, Momordica charantia; Lythraceae weeds: Lythrum salicaria; Apiaceae weeds: Hydrocotyle sibthorpioides; Sapindaceae weeds: Cardiospermum halicacabum; Primulaceae weeds: Anagallis arvensis; Asclepiadaceae weeds: Asclepias syriaca, Ampelamus albidus; Rubiaceae weeds: Galium aparine, Galium spurium var. echinospermon, Spermacoce latifolia, Richardia brasiliensis, Borreria alata; Convolvulaceae weeds: Ipomoea nil, Ipomoea hederacea, Ipomoea purpurea, Ipomoea hederacea var. integriuscula, Ipomoea lacunosa, Ipomoea triloba, Ipomoea acuminata, Ipomoea hederifolia, Ipomoea coccinea, Ipomoea quamoclit, Ipomoea grandifolia, Ipomoea aristolochiafolia, Ipomoea cairica, Convolvulus arvensis, Calystegia hederacea, Calystegia japonica, Merremia hedeacea, Merremia aegyptia, Merremia cissoides, Jacquemontia tamnifolia; Boraginaceae weeds: Myosotis arvensis; Lamiaceae weeds: Lamium purpureum, Lamium amplexicaule, Leonotis nepetaefolia, Hyptis suaveolens, Hyptis lophanta, Leonurus sibiricus, Stachys arvensis; Solanaceae weeds: Datura stramonium, Solanum nigrum, Solanum Americanum, Solanum ptycanthum, Solanum sarrachoides, Solanum rostratum, Solanum aculeatissimum, Solanum sisymbriifolium, Solanum carolinense, Physalis angulata, Physalis subglabrata, Nicandra physaloides; Scrophulariaceae weeds: Veronica hederaefolia, Veronica persica, Veronica arvensis; Plantaginaceae weeds: Plantago asiatica; Asteraceae weeds: Xanthium pensylvanicum, Xanthium occidentale, Helianthus annuus, Matricaria chamomilla, Matricaria perforata, Chrysanthemum segetum, Matricaria matricarioides, Artemisia princeps, Artemisia vulgaris, Artemisia verlotorum, solidago altissima, Taraxacum officinale, Galinsoga ciliata, Galinsoga parviflora, Senecio vulgaris, Senecio brasiliensis, Senecio grisebachii, Conyza bonariensis, Conyza canadensis, Ambrosia artemisiaefolia, Ambrosia trifida, Bidens pilosa, Bidens frondosa, Bidens subalternans, Cirsium arvense, Cirsium vulgare, Silybum marianum, Carduus nutans, Lactuca serriola, Sonchus oleraceus, Sonchus asper, Wedelia glauca, Melampodium perfoliatum, Emilia sonchifolia, Tagetes minuta, Blainvillea latifolia, Tridax procumbens, Porophyllum ruderale, Acanthospermum australe, Acanthospermum hispidum, Cardiospermum halicacabum, Ageratum conyzoides, Eupatorium perfoliatum, Eclipta alba, Erechtites hieracifolia, Gamochaeta spicata, Gnaphalium spicatum, Jaegeria hirta, Parthenium hysterophorus, Siegesbeckia orientalis, Soliva sessilis; Liliaceae weeds: Allium canadense, Allium vineale;

Commelinaceae weeds: Commelina communis, Commelina bengharensis, Commelina erecta; Poaceae weeds: Echinochloa crus-galli, Setaria viridis, Setaria faberi, Setaria glauca, Setaria geniculata, Digitaria ciliaris, Digitaria sanguinalis, Digitaria horizontalis, Digitaria insularis, Eleusine indica, Poa annus, Alospecurus aequalis, Alopecurus myosuroides, Avena fatua, Sorghum halepense, Sorghum vulgare, Agropyron repens, Lolium multiflorum, Lolium perenne, Lolium rigidum, Bromus secalinus, Bromus tectorum, Hordeum jubatum, Aegilops cylindrica, Phalaris arundinacea, Phalaris minor, Apera spica-venti, Panicum dichotomiflorum, Panicum texanum, Panicum maximum, Brachiaria platyphylla, Brachiaria ruziziensis, Brachiaria plantaginea, Brachiaria decumbens, Brachiaria brizantha, Brachiaria humidicola, Cenchrus echinatus, Cenchrus pauciflorus, Eriochloa villosa, Pennisetum setosum, Chloris gayana, Eragrostis pilosa, Rhynchelitrum repens, Dactyloctenium aegyptium, Ischaemum rugosum, Oryza sativa, Paspalum notatum, Paspalum maritimum, Pennisetum clandestinum, Pennisetum setosum, Rottboellia cochinchinensis; Cyperaceae weeds: Cyperus microiria, Cyperus iria, Cyperus odoratus, Cyperus rotundus, Cyperus esculentus, Kyllinga gracillima, Equisetaceae weeds: Equisetum arvense, Equisetum palustre, Trianthema weeds and the like.

The herbicidal combination of the present invention maybe used to control the target weeds among the crops such as GMO (Genetically Modified Organism) and Non GMO varieties of Cotton (*Gossypium* spp.), Paddy (*Oryza sativa*), Wheat (*Triticum aestavum*), Barley (*Hordeum vulgare*), Maize (*Zea mays*), Sorghum (*Sorghum bicolor*), Oat (*Avena sativa*), Pearl millet (*Pennisetum glaucum*), Sugarcane (*Saccharum officinarum*), Sugarbeet (*Beta vulgaris*), Soybean (*Glycin max*), Peanut (*Arachis hypogaea*), Sunflower (*Helianthus annuus*), Mustard (*Brassica juncea*), Rape seed (*Brassica napus*), Linseed (*Linum usitatissimum*), Sesame (*Sesamum indicum*), Green gram (*Vigna radiata*), Black gram (*Vigna mungo*), Chickpea (*Cicer aritinum*), Cowpea (*Vigna unguiculata*), Redgram (*Cajanus cajan*), Frenchbean (*Phaseolus vulgaris*), Indian bean (*Lablab purpureus*), Horse gram (*Macrotyloma uniflorum*), Field pea (*Pisum sativum*), Cluster bean (*Cyamopsis tetragonoloba*), Lentils (*Lens culinaris*), Brinjal (*Solanum melongena*), Cabbage (*Brassica oleracea var. capitata*), Cauliflower (*Brassica oleracea var. botrytis*), Okra (*Abelmoschus esculentus*), Onion (*Allium cepa L.*), Tomato (*Solanum lycopersicun*), Potato (*Solanum tuberosum*), Sweet potato (*Ipomoea batatas*), Chilly (*Capsicum annum*), Garlic (*Allium sativum*), Cucumber (*Cucumis sativus*), Muskmelons (*Cucumis melo*), Watermelon (*Citrullus lanatus*), Bottle gourd (*Lagenaria siceraria*), Bitter gourd (*Momordica charantia*), Radish (*Raphanus sativus*), Carrot (*Dacus carota subsp. sativus*), Turnip (*Brassica rapa subsp rapa*), Apple (*Melus domestica*), Banana (*Musa spp.*), Citrus groups (*Citrus spp.*), Grape (*Vitis vinifera*), Guava (*Psidium guajava*), Litchi (*Litchi chinensis*), Mango (*Mangifera indica*), Papaya (*Carica papaya*), Pineapple (*Ananas comosus*), Pomegranate (*Punica granatum*), Sapota (Manilkara zapota), Tea (*Camellia sinensis*), Coffea (*Coffea Arabica*), Turmeric (*Curcuma longa*), Ginger (*Zingiber officinale*), Cumin (*Cuminum cyminum*), Fenugreek (*Trigonella foenum-graecum*), Fennel (*Foeniculum vulgare*), Coriander (*Coriandrum sativum*), Ajwain (*Trachyspermum ammi*), Psyllium

(*Plantago ovate*), Black Pepper (*Piper nigrum*), Stevia (*Stevia rebaudiana*), Safed musli (*Chlorophytum tuberosum*), Drum stick (*Moringa oleifera*), Coconut (*Coco nucifera*), Mentha (*Mentha spp.*), Rose (*Rosa spp.*), Jasmine (*Jasminum spp.*), Marigold (*Tagetes spp.*), Common daisy (*Bellis perennis*), Dahlia (*Dahlia hortnesis*), Gerbera (*Gerbera jamesonii*), Carnation (*Dianthus caryophyllus*).

In an embodiment, the individual components of the combination of the present invention may be applied to the locus either simultaneously or sequentially, such that bispyribac or bispyribac-sodium and imazethapyr may be applied in a tank mix or as a pre-mixed composition.

In an embodiment, combination of the present invention may be applied either pre- or post emergent. In a preferred embodiment, the combination of the present invention may be used pre-emergent, and pre-plant. The advantage of the combination is surprisingly good residual effects, and quick burndown of the weeds when applied pre-plant or pre-emergent.

The method of control of the present invention may be carried out by spraying the suggested tank mixes, or the individual herbicides may be formulated as a kit-of-parts containing various components that may be mixed as instructed prior to spraying.

In an embodiment the components of the present invention may be packaged such that bispyribac or bispyribac-sodium and imazethapyr may be packaged separately and then tank mixed before the spraying.

In another embodiment the components of the present invention may be packaged such that bispyribac or bispyribac-sodium and imazethapyr may be packaged separately, whereas other additives are packaged separately, such that the two maybe tank mixed at the time of spraying.

In another embodiment the components of the present invention may be packaged as composition such that the bispyribac or bispyribac-sodium and imazethapyr are formulated into one composition and other additives and bispyribac or bispyribac-sodium and imazethapyr are packaged separately, such that the two may be tank mixed at the time of spraying.

In an embodiment, the pyrimidinyl benzoate derivative e.g. bispyribac-sodium may be present in an amount of from about 1 g/ha to about 1000 g/ha.

In an embodiment, the imidazolinone derivative e.g. imazethapyr may be present in an amount of from about 1 g/ha to about 1000 g/ha.

The herbicidal combination of the present invention wherein combination is applied in an amount of from 30 to 800 g a.i./ha, preferably from 30 to 650 g a.i./ha and more preferably from 30 to 500 g a.i./ha.

The herbicidal combination of the present invention, wherein combination is used to provide a rate of application of from 0.01 to 100 liter/ha, preferably from 0.01 to 80 liter/ha, and more preferably from 0.01 to 40 liter/ha.

Thus, in another aspect, the present invention provides a method of controlling weeds at a locus, said method comprising applying a composition comprising bispyribac or bispyribac-sodium and imazethapyr and at least one agrochemically acceptable excipient.

Surprisingly, it has been found by the present inventors that bispyribac or bispyribac-sodium and imazethapyr, when applied individually, was ineffective in the control of weeds, but demonstrated excellent synergistic control on weeds when applied together. The combination controlled the weed both pre and post emergently, but was particularly good in the control of burndown weeds. The combination of bispyribac or bispyribac-sodium and imazethapyr synergistically controlled broadleaf weeds, sedges, and grasses a particular locus. The current invention therefore provides advantageous methods of controlling weeds both pre and post emergently. The present method also provides a broader spectrum of controlling weeds that helps in resistance management, thus preventing the weed from becoming resistant to either of the herbicides whist providing a broader spectrum of control at lower use rates.

EXAMPLES:

The present invention is further illustrated by the following examples. These examples describe possible preferred embodiments for illustrative purposes only, but they do not limit the scope of the invention. These laboratory scale experiments can be scaled up to industrial/ commercial scale.

Example 1 and 2: Water Dispersible Granule (WDG/WG)

	Example 1	**Example 2**
Ingredients	**Concentration (45% w/w)**	**Concentration (60% w/w)**
Bispyribac-sodium	9	15
Imazathpyr	36	45
Sodium lauryl sulphate	5	8
Sodium lignosulfonate	10	12
Kaolin	25	6
Carboxymethyl cellulose	5	1
Sodium sulphate	10	9
Precipitated silica	0	4
Total	100	100

Process for preparation: A process for preparing a herbicidal formulation in the form of a water dispersible granules; comprising the steps of:

a) mixing bispyribac-sodium and imazethapyr, sodium lauryl sulphate, sodium lignosulfonate, kaolin, carboxymethyl cellulose, and precipitated silica in a blender to form a homogenous mass;

b) milling the homogenous mass to obtain particle size below 10 microns;

c) preparing a dough using the above milled material by using 10 to 20% water;

d) extruding the dough using a extruder having a suitable screen by maintaining the temperature of the screen below 50°C to obtain extruded granules;

e) drying the extruded granules using a fluid bed dryer by keeping air flow at 75% to 80% and maintaining the temperature of the air at 50°C to obtain free flowing WDG/WG formulation.

Example 3 and 4: Suspension Concentrate (SC)

	Example 3	**Example 4**
Ingredients	**Concentration (20% w/w)**	**Concentration (40% w/w)**
Bispyribac-sodium	4	8
Imazathpyr	16	32
Atlox 4913	4	8
Atlox 4894	6	0
Atlas 5000G	0	8
Ufoxane 3A	4	4
Precipitated silica	2	2
Xanthan gum	0.4	0.4
Proxel GXL	0.5	0.5
Water	q.s.	q.s.
Total	100	100

Process for preparation: A process for preparing a herbicidal formulation in the form of a suspension concentrate; comprising the steps of:

a) All the ingredients were weighed as per Example 1 and Example 2, then preparing a slurry by adding Atlox 4913, Atlox 4894, Atlas 5000G, Ufoxane 3A, precipitated silica and active ingredients (bispyribac-sodium and imazethapyr) in water;

b) milling the slurry to achieve desired particle size below 10 microns;

c) separately, preparing a gel by adding thickening agent such as xanthan gum, and Proxel GXL; and

d) adding gel to the step c) slurry to obtain said stable liquid composition. The formulation is physically stable and easy to use in the fields.

Example 5: Wettable powder (80 % w/w WP)

Ingredients	**Concentration (80% w/w)**
Bispyribac-sodium	32
Imazathpyr	48
Sodium lauryl sulphate	6
Sodium lignosulfonate	8
Kaolin	5
Moisture	1
Total	100

Example 6 and 7: Water Dispersible Granule (WDG)

	Example 6	Example 7
Ingredients	**Concentration (60% w/w)**	**Concentration (60% w/w)**
Bispyribac-sodium	10	15
Imazapic	50	0
Imazaquin	0	35
Sodium lauryl sulphate	10	12
Sodium lignosulfonate	12	20
Silica	8	5
Clay	10	13
Total	100	100

Synergy Studies:

The present invention provides a method of inhibiting different weeds flora in rice wherein the treatment comprises the combination of two herbicides technical i.e. Bispyribac-sodium and Imazethapyr.

Methodology:

Study was conducted on combination of two different compounds i.e. Bispyribac-sodium and Imazethapyr. For the study *Echinochloa colona*, *Echinochloa Crus-galli, Leptochloa chinensis, Cyperus iria Cyperus difformis, Fimbristylis Spp., Monochoria vaginalis, Eclipta alba, Ludwigia Spp., Sagittaria Spp.* and *Marsilea Spp.* seeds were sown into the seedling trays and regular watering was done. At two to three leaf stage of test weeds herbicides were sprayed in the booth of Generation III research sprayer (to obtain uniformity in spray) with a delivery rate of about 500 L/hectare of spray solution through flat fan nozzle at a pressure of 25-30 psi. Treatments details are given in Table A. After application all the trays were kept at 25 ± 3 degree centigrade in greenhouse. The efficacy of all the treatments was evaluated at 15 days after application (DAA). The observation recorded was based on weed mortality rate in percentage by comparing it with untreated control. To know the Synergistic effect of combination of both compounds the expected value was calculated.

Table A: Treatment details

Sr.No.	Treatment	Doses (g a.i./ha)
1	Bispyribac-sodium	25
2	Imazethapyr	75
3	Imazethapyr	100
4	Bispyribac-sodium + Imazethapyr	25 + 75
5	Bispyribac-sodium + Imazethapyr	25 +100
6	Control	NA

Synergistic effect calculation (Colby's equation):

The expected activity for a given combination of two active compounds (binary composition) can be calculated as follows:

$$E = X + Y - \frac{XY}{100}$$

wherein,

E represents the expected percentage of inhibition of the disease/weed control for the combination of two herbicides at defined doses (for example equal to X and Y, respectively), X is the percentage of inhibition observed for the weed by the compound (1) at a given dose (equal to X), Y is the percentage of inhibition observed for the weed by the compound (2) at a defined dose (equal to y).

When the percentage of inhibition observed for the combination is greater than E, there is a synergistic effect.

Phytotoxicity Study:

In order to determine the phytotoxicity effect of herbicides on the rice, Sona Masuri variety of rice (Imazethapyr non-tolerant rice variety) was sown and at three to four leaf stage herbicides were sprayed in Generation III research sprayer.

Any visual injury/ phytotoxicity was assessed on the crop at 15 DAA based on chlorosis, necrosis, wilting and stunting. Injury rating was recorded on a scale of 0-100, where 0 means no injury to crop and 100 means complete plant death.

Residual effect:

To check the residual effect of treatments all the weeds were sown in their respective seedling trays after one day of application. The observation was recorded in the form of germination percentage and visual biomass reduction in comparison to control at interval of 15 and 30 days after application.

Results:

Effect on weed:

At 15 DAA Bispyribac-sodium + Imazethapyr treatments recorded highest efficacy (Table B, Table D, and Table F) against all the test weeds i.e. *Echinochloa colona*, *Echinochloa Crus-galli, Leptochloa chinensis, Cyperus iria Cyperus difformis, Fimbristylis Spp., Monochoria vaginalis, Eclipta alba, Ludwigia Spp., Sagittaria Spp.* and *Marsilea Spp.* Application of Bispyribac-sodium + Imazethapyr indicated surprising synergies in controlling the test weeds. (Table C, Table E, and Table G).

Table B: Weed control in percentage in Grass

Treatment	Doses/ ha	Percent Weed control

	g a.i./ha	*Eichochloa colonum*	*Eichochloa crusgalli*	*Leptochloa chinensis*
Bispyribac-sodium	25	72.7	57.7	28.0
Imazethapyr	75	62.0	65.3	67.3
Imazethapyr	100	74.0	67.0	72.3
Bispyribac-sodium + Imazethapyr	25 + 75	90.7	89.7	86.0
Bispyribac-sodium + Imazethapyr	25 +100	95.3	94.0	92.0
Control	NA	0.0	0.0	0.0

Table C: Synergistic response calculation (Colby's Method)

Treatment	**Doses/ ha**	**Expected response calculation**		
	g a.i./ha	*Eichochloa colonum*	*Eichochloa crusgalli*	*Leptochloa chinensis*
Bispyribac-sodium + Imazethapyr	25 + 75	89.6 (+1.1)	85.3 (+4.3)	76.5 (+9.5)
Bispyribac-sodium + Imazethapyr	25 +100	92.9 (+2.4)	86.0 (+8.0)	80.1 (+11.9)

Expected responses for the mixtures are shown in Table C following difference between observed (Table B) and expected values are shown in the parenthesis by a plus (+) sign to indicate synergism.

Table D: Weed control in percentage in Sedges

Treatment	**Doses/ ha**	**Percent Weed control**		
	g a.i./ha	*Cyperus irria*	*Cyperus difformis*	*Fimbristylis Spp.*
Bispyribac-sodium	25	66.3	64.0	70.0
Imazethapyr	75	*63.3*	*65.0*	*70.7*

Imazethapyr	100	69.3	70.0	74.7
Bispyribac-sodium + Imazethapyr	25 + 75	89.0	90.3	95.0
Bispyribac-sodium + Imazethapyr	25 + 100	94.7	96.3	96.7
Control	NA	0.0	0.0	0.0

Table E: Synergistic response calculation (Colby's Method)

Treatment	**Doses/ ha**	**Expected response calculation**		
	g a.i./ha	*Cyperus irria*	*Cyperus difformis*	*Fimbristylis Spp.*
Bispyribac-sodium + Imazethapyr	25 + 75	87.7 (+1.3)	87.4 (+2.9)	95.0 (+3.8)
Bispyribac-sodium + Imazethapyr	25 +100	89.7 (+5.0)	89.2 (+7.1)	96.7 (+4.3)

Expected responses for the mixtures are shown in Table E following difference between observed (Table D) and expected values are shown in the parenthesis by a plus (+) sign to indicate synergism.

Table F: Weed control in percentage in Broad Leaves

Treatment	**Doses/ ha**	**Percent Weed control**				
	g a.i./ha	*Monochoria vaginalis*	*Eclipta alba*	*Ludwigia Spp.*	*Sagittaria Spp.*	*Marsilea Spp.*
Bispyribac-sodium	25	69.3	72.3	74.0	63.3	65.0
Imazethapyr	75	70.7	69.7	70.0	71.0	80.3
Imazethapyr	100	72.7	73.3	76.3	74.0	85.0
Bispyribac-sodium + Imazethapyr	25 + 75	93.7	92.3	93.0	92.0	95.0

Bispyribac-sodium + Imazethapyr	25 +100	96.7	97.0	97.3	95.7	97.3
Control	NA	0.0	0	0.0	0	0.0

Table G: Synergistic response calculation (Colby's Method)

Treatment	**Doses/ ha**	**Expected response calculation**				
	g a.i./ha	*Monochoria vaginalis*	*Eclipta alba*	*Ludwigia Spp.*	*Sagittaria Spp.*	*Marsilea Spp.*
Bispyribac-sodium + Imazethapyr	25 + 75	91.0 (+2.7)	91.6 (+0.7)	92.2 (+0.8)	89.4 (+2.6)	93.1 (+1.9)
Bispyribac-sodium + Imazethapyr	25 +100	91.6 (+5.0)	92.6 (+4.4)	93.8 (+3.5)	90.5 (+5.2)	94.8 (+2.6)

Expected responses for the mixtures are shown in Table G following difference between observed (Table F) and expected values are shown in the parenthesis by a plus (+) sign to indicate synergism.

Phytotoxicity:

Severe phytotoxicity was observed 95% and 100% in Imazethapyr 75 g ai/ha and 100 g ai/ha, respectively. Even mixture combination involving Imazethapyr indicated similar phytotoxic effects on rice plants. Bispyribac-sodium @ 25 g ai/ha was highly selective to rice and did not show any phytotoxicity.

Table H: Phytotoxicity on rice plant

Treatment	**Dose/ ha**	**Phytotoxicity (%)**
	g a.i./ha	**Visual observation (0-100 scale)**
Bispyribac-sodium	25	0.0
Imazethapyr	75	95
Imazethapyr	100	100
Bispyribac-sodium + Imazethapyr	25 + 75	95
Bispyribac-sodium + Imazethapyr	25 +100	95

Control	NA	0.0

Residual effect:

In Imazethapyr treated seedling trays, fresh germination of test weeds was only 10 % and biomass of the germinated weeds was reduced drastically more than 80 % to comparison to control. A similar trend was observed in Bispyribac-sodium + Imazethapyr mixture treatments. Bispyribac-sodium solo treatments had no residual efficacy.

While the foregoing written description of the invention enables one of ordinary skill to make and use what is considered presently to be the best mode thereof, those of ordinary skill will understand and appreciate the existence of variations, combinations, and equivalents of the specific embodiment, method, and examples herein. The invention should therefore not be limited by the above described embodiment, method, and examples, but by all embodiments and methods within the scope and spirit of the invention.

CLAIMS:

1. A herbicidal combination comprising:
    a) a pyrimidinyl benzoate derivative; and
    b) an imidazolinone derivative,

wherein the weight ratio of herbicide (a) to herbicide (b) is from 1:100 to 100:1.

2. The herbicidal combination as claimed in claim 1, wherein said pyrimidinyl benzoate derivative is selected from the group consisting of bispyribac, bispyribac-sodium, pyribenzoxim, pyriftalid, pyriminobac, pyriminobac-methyl, and combination thereof.
3. The herbicidal combination as claimed in claim 1, wherein said imidazolinone derivative is selected from the group consisting of imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin, imazethapyr and combination thereof.
4. The herbicidal combination as claimed in claim 1, wherein said combination comprising:
    a) bispyribac, bispyribac-sodium;
    b) imidazolinone derivative is selected from the group consisting of imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazapyr, imazaquin, imazethapyr and combination thereof.
5. The herbicidal combination as claimed in claim 1, wherein the weight ratio of herbicide (a) to herbicide (b) is in the range from 1:80 to 80:1, more preferably 1:10 to 10:1, and most preferably 1:4 to 4:1.
6. The herbicidal combination as claimed in claim 3 or 4, wherein said imazethapyr is in crystalline form 1 or crystalline form 2.
7. The herbicidal combination as claimed in claim 1, wherein said combination further comprises at least one insecticide(s), fungicide(s), acaricide(s), nematicide(s), herbicide(s), safener(s), plant growth regulator(s), biostimulant(s) and combination thereof.
8. A herbicidal composition comprising an herbicidal combination as claimed in any one of claims 1 to 7, and an agrochemically acceptable excipient(s).
9. The herbicidal composition as claimed in claim 8, wherein said agrochemically acceptable excipient(s) comprises solid carrier(s), liquid carrier(s), gaseous carrier(s), surfactant(s), binder(s), disintegrating agent(s), antioxidant(s), osmotic agent(s), wetting agent(s), pH adjuster(s), thickener(s), preservative(s), filler(s), diluent(s), emulsifier(s), anti-caking agent(s), anti-freezing agent(s), defoaming agent(s), viscosifying agent(s), extender(s), buffering agent(s), solubilizer(s), chelating agent(s), stabilizer(s) and/or coloring agent(s) or combination thereof.
10. The herbicidal composition as claimed in claim 8, wherein said composition is formulated as a dusts, a microcapsules, a solutions, a suspension concentrate (SC), a water dispersible granule (WDG)/(WG), a tablet (TB), a wettable powder (WP), a water dispersible tablet (WT), an ultra-low volume (ULV) liquid (UL), an ultra-low volume (ULV), a suspension (SU), a water soluble powder

(SP), a suspo-emulsion (SE), a granule (GR), an oil-in-water emulsion (EW), an emulsifiable granule (EG), an emulsion oil in water (EO), an emulsifiable powder (EP), an emulsion for seed treatment (ES), a solution for seed treatment (LS), a flowable concentrate for seed treatment (FS), an emulsifiable concentrate (EC), a micro-emulsion (ME), oil-in-water emulsions (EW), an oil miscible flowable concentrate (oil miscible suspension) (OF), an oil dispersible powder (OP), an oil dispersion (OD), a capsule suspension (CS), a dustable powder (DP), a soluble concentrate (SL), a water soluble granule (SG), an aerosol (AE), a mixed formulation of CS and SL, a mixed formulation of CS and SC (ZC), a mixed formulation of CS and SE (ZE), or a mixed formulation of CS and EW (ZW).

11. The herbicidal composition as claimed in claim 8 or 10, wherein said composition is formulated as a water dispersible granule (WDG)/(WG), a wettable powder (WP), or a suspension concentrate (SC).

12. The herbicidal composition as claimed in any one of claims 8 to 11, wherein said combination is used to provide a rate of application of from 0.01 to 100 liter/ha.

13. The herbicidal composition as claimed in any one of claims 8 to 11, wherein said combination is applied in an amount of from 30 to 800 g a.i./ha.

14. The herbicidal composition as claimed in any one of claims 1 to 13, for controlling undesirable vegetation in crop plants.

15. A method of controlling weeds which comprises contacting the vegetation or the locus thereof with or applying an herbicidal combination as claimed in claim 1, to the soil or water to prevent the emergence or growth of vegetation.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IB2022/061120

A. CLASSIFICATION OF SUBJECT MATTER
A01N43/54,A01N43/40 Version=2023.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N

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.
X	AU2012202066C1 (KUMIAI CHEMICAL INDUSTRY CO LTD [JP]) 05 SEPTEMBER 2013 (05-09-2013) abstract, claims 1-15, page 55, lines 11-22; page 63, lines 2-7	1-15
X	CN107236547A (ANHUI SHENGDAN BIOCHEMICAL CO LTD) 10 OCTOBER 2017 (10-10-2017) examples 3-5	1-15

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

* Special categories of cited documents:
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Date of the actual completion of the international search	Date of mailing of the international search report
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