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(71) Applicant: QUENA PLANT PROTECTION N.V.

[NL/NL]; Pos Cabai Office Park, Unit 13, P.O. Box 403, Curacao (NL).

(72) Inventor: GOLDSHMIDT, Josef; 23 HaAlon Street,

7313000 Moshav Gimzo (IL).

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(54) Title: HERBICIDAL MIXTURE OF IMAZETHAPYR AND PROPAQUIZAFOP

(57) Abstract: A synergistic herbicidal mixture for controlling undesired vegetation comprising imazethapyr and propaquizafop, esters, salts and/or combination thereof.



HERBICIDAL MIXTURE OF IMAZETHAPYR AND PROPAQUIZAPOP

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of Indian Provisional Application No. 5 524/KOL/2013, filed May 8, 2013, which is hereby incorporated by reference herein in its entirety.

FIELD

The present subject matter relates to a herbicidal mixture for controlling undesired vegetation. Specifically, the present subject matter relates to a herbicidal 10 mixture comprising a synergistic combination of propaquizafop and imazethapyr.

BACKGROUND

The control of undesired vegetation is extremely important in order to achieve high crop efficiency. In many cases, herbicides have an effect against a spectrum of 15 weeds; however, these herbicides may not be effective certain type of other weeds, which may also be present in the crop to be protected. Therefore, there is a strong need for mixing two or more herbicides.

Mixtures of selected herbicides have several advantages over the use of a single herbicide including (a) an increase in the spectrum of weeds controlled or an extension 20 of weed control over a longer period of time, (b) an improvement in crop safety by using minimum doses of selected herbicides applied in combination rather than a single high dose of one herbicide and (c) a delay in the appearance of resistant weed species to selected herbicides {*Int. J. Agri. Biol.*, Vol. 6, No. 1, 2004, pages 209-212}.

However, the activity and selectivity behavior of a mixture is difficult to predict 25 since the behavior of each single herbicide in the mixture is often affected by the presence of the other(s) and the activity of the mixture may also vary considerably depending on chemical character, plant species, growth stage, and environmental conditions, mostly this practice results in reduced activity of the herbicides in the mixture.

30 Propaquizafop, ((R)-2-[[[(1-methylethylidene)amino]oxy]ethyl 2-[4-[(6-chloro-2-quinoxalinyloxy]phenoxy]propanoate)], disclosed in US4545807, is a Fatty acid synthesis inhibitor which inhibits acetyl CoA carboxylase (ACCase). It is a systemic

post-emergence herbicide absorbed by foliage and roots, and translocated throughout the plant. Propaquizafop is used for the control of a wide range of annual and perennial grasses (including *Sorghum halepense*, *Agropyron repens* and *Cynodon dactylon*) in soya beans, cotton, sugar beet, potatoes, peanuts, peas, oilseed rape and vegetables.

5 Imazethapyr, (R5)-5-ethyl-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl) nicotinic acid, disclosed in US 4,798,619, is a branched chain amino acid synthesis (ALS or AHAS) inhibitor. Hence reduces levels of valine, leucine and isoleucine, leading to disruption of protein and DNA synthesis. Imazethapyr is a systemic herbicide, absorbed by the roots and foliage. Imazethapyr control many major annual
10 and perennial grass and broad leaved weeds.

 According to Herbicide Mixture Compatibility Chart, published by the government of Western Australia, Department of agriculture and food Tank, mixing imazethapyr and propaquizafop is not recommended. The chart teaches that excessive crop damage or reduction in weed control may occur by the combination of both
15 herbicides

[www.agric.wa.gov.au/objtwr/imported_assets/content/pw/weed/herbicide%20compatibility%20chart.pdfj].

 In addition, Paul F. Myers and Harold D. Coble {*Weed Technology Vol. 6, No. 2, 1992, pp. 333-338*) teaches that tank-mix combinations of imazethapyr with clethodim,
20 fluazifop-P, quizalofop, or sethoxydim, all inhibitors of acetyl CoA carboxylase similar to propaquizafop, resulted in an antagonistic interaction.

SUMMARY

 The subject matter relates to a herbicidal mixture comprising imazethapyr and
25 propaquizafop, esters, salts and/or combination thereof. According to an embodiment, the weight ratio of imazethapyr to propaquizafop may be from 20:1 to 1:20 In a specific embodiment, the weight ratio of imazethapyr to propaquizafop may be from 5:1 to 1:5.

 According to an embodiment, the compounds of the mixture may be applied jointly or in a succession. The application rate of the mixture may be from 0.1 liter/ha to
30 10 liter/ha. In a specific embodiment, the application rate of the mixture may be 1.25 liter/ha. The mixture may be applied in an amount of 125 g/ha. The amount of

imazethapyr to be applied may be 75 g/ha and the amount of propaquizafop may be 50 g/ha.

According to another aspect of the described subject matter provided herein, a composition comprising imazethapyr and propaquizafop, esters, salts or combination thereof and at least one agriculturally acceptable carrier. The composition may further include at least one surfactant, solid diluent, liquid diluent, or a combination thereof.

According to yet another aspect there is provided a method of controlling undesired vegetation comprising applying to the locus of the undesired vegetation a herbicidally effective amount of the mixture comprising imazethapyr, propaquizafop esters, salts and/or combination thereof. The crop may be selected from the group consisting of soybeans, blackgram, peanuts, green gram, pigeon pea, beans, field peas and cluster beans. In an embodiment the mixture may be applied in an amount of 1 to 500 g/ha. In a preferred embodiment, the mixture may be applied in an amount of 125 g/ha.

The undesired vegetation may be selected from the group consisting of *Echinochloa Colona*, *Dinebra Arabica*, *Cynotis sp*, *Eleusine Indica*, *Cynodon Dactylon*, *Euphorbia Hirta*, *Amaranthus Viridis*, *Digera Arvensis*, *Digera sp.*, *Panicum sp.*, *Phyllanthus sp*, *Commelina benghalensis L*, *Parthenium*, *Trianthema Portulacasturm*, *Cleome viscosa*, *Digera arvensis*, *Parthenium hysterophorus*, *Cynadon dactylone*, *Commelina bengalensis* and *Dinebra sp.*, *Portulaca sp.*, *Trianthima sp.*, *Dactyloctenium aegyptium*, *Corchprus sp.*, *Trianthema monogyna*, *Brachiaria sp.*

According to yet another aspect there is provided a method of controlling undesired vegetation comprising applying to the locus of the undesired vegetation a herbicidally effective amount of the composition comprising imazethapyr, propaquizafop esters, salts and/or combination thereof.

According to yet another aspect there is provided a synergistic mixture comprising imazethapyr and propaquizafop, esters, salts and/or combination thereof.

DETAILED DESCRIPTION

All technical and scientific terms used herein have the same meanings as commonly understood by someone ordinarily skilled in the art to which the present subject matter belongs. The following definitions are provided for clarity.

As used herein the term "crop" includes reference to whole plant, plant organ (e.g., leaves, stems, twigs, roots, trunks, limbs, shoots, fruits etc.), or plant cells.

As used herein the term "locus" includes not only areas where weeds may already be growing, but also areas where weeds have yet to emerge, and also to areas
5 under cultivation.

As used herein the term "agriculturally acceptable carrier" means carriers of which are known and accepted in the art for the formation of formulations for agricultural or horticultural use.

The term "surfactant," as used herein, refers to an agriculturally acceptable
10 material which imparts emulsifiability, stability, spreading, wetting, dispersibility or other surface-modifying properties.

The term "a" or "an" as used herein includes the singular and the plural, *unless specifically* stated otherwise. Therefore, the term "a," "an," or "at least one" can be used interchangeably in this application.

Throughout the application, descriptions of various embodiments use the term
15 "comprising;" however, it will be understood by one of skill in the art, that in some specific instances, an embodiment can alternatively be described using the language "consisting essentially of" or "consisting of."

For the purposes of better understanding the present teachings and in no way
20 limiting the scope of the teachings, unless otherwise indicated, all numbers expressing quantities, percentages or proportions, and other numerical values used in the specification and claims, are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may
25 vary depending upon the desired properties sought to be obtained. At the very least, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

The present subject matter relates to a herbicidal mixture comprising imazethapyr and propaquizafop, esters, salts and/or combination thereof.

30 An embodiment relates to a synergistic herbicidal mixture comprising imazethapyr and propaquizafop, esters, salts and/or combination thereof.

In an embodiment, the weight ratio of imazethapyr to propaquizafop in the mixture may be from about 50:1 to 1:50. In another embodiment, the weight ratio of imazethapyr to propaquizafop may be from about 20:1 to 1:20. In yet another embodiment, the weight ratio of imazethapyr to propaquizafop may be from about 5:1 to 1:5. In yet another embodiment, the weight ratio of imazethapyr to propaquizafop may be from about 1.75:1 to 1:1.75. In yet another embodiment, the weight ratio of imazethapyr to propaquizafop may be from about 1.5:1 to 1:1.5. In yet another embodiment, the weight ratio of imazethapyr to propaquizafop may be from about 1.4:1 to 1:1.4. In yet another embodiment, the weight ratio of imazethapyr to propaquizafop may be from about 1.2:1 to 1:1.2.

In a specific embodiment, the weight ratio of imazethapyr to propaquizafop may be about 1.1:1.

In another embodiment, a composition comprising imazethapyr and propaquizafop including esters and salts thereof and an agriculturally acceptable carrier, is provided.

In yet another embodiment, the composition comprising at least one additional component selected from the group of surfactants, solid diluents and liquid diluents.

The herbicidal compositions and herbicidal mixtures may be applied jointly or in a succession.

The compositions may include additional other crop protection agents, for example pesticides, safeners or agents for controlling phytopathogenic fungi or bacteria.

In an embodiment, the herbicidal mixture may be applied in an amount of about 0.1 to 500 liter/ha. In yet another embodiment, the herbicidal mixture may be applied in an amount of about 0.1 to 100 liter/ha. In another embodiment, the herbicidal mixture may be applied in an amount of about 0.1 to 10 liter/ha. In a specific embodiment, the mixture may be applied in an amount of about 1.25 liter/ha (equal to 0.50 liter/acre). In yet another specific embodiment, the mixture may be applied in an amount of about 1.35 liter/ha (equal to 0.55 liter/acre). In yet another specific embodiment, the mixture may be applied in an amount of about 1.50 liter/ha (equal to 0.60 liter/acre). In a specific embodiment, the mixture may be applied in an amount of about 2.00 liter/ha (equal to 0.80 liter/acre). In yet another specific embodiment, the mixture may be applied in an amount of about 2.25 liter/ha (equal to 0.90 liter/acre). In yet another specific

embodiment, the mixture may be applied in an amount of about 2.50 liter/ha (equal to 1.00 liter/acre).

According to an embodiment, the herbicidal mixture may be applied in an amount of about 1 to 1000 g/ha. In another embodiment, the herbicidal mixture may be applied in an amount of about 1 to 500 g/ha. In a specific embodiment, the mixture may be applied in an amount of about 125 g/ha. Correspondingly, the amount of imazethapyr is about 75 g/ha and propaquizafop is about 50 g/ha.

Additionally, a method of controlling undesired vegetation comprising applying to the locus of the undesired vegetation a herbicidally effective amount of a mixture of imazethapyr and propaquizafop, esters, salts and/or combination thereof, is provided.

The mixtures and/or the herbicidal compositions may be applied pre-plant incorporated, pre- or post-emergence.

In an embodiment, the mixture may be applied on crops which include soybeans, blackgram, peanuts, green gram, pigeon pea, cluster beans, field peas, mung beans, dry beans, peanuts, groundnuts, snap bean, alfalfa, lettuce, beans. In a specific embodiment the crop includes soybeans, groundnuts, blackgram, peanuts, green gram, pigeon pea, beans, field peas and cluster beans. In an embodiment, the mixture may be applied on tolerant or resistant mutants or transgenic crops plants such as soybean, and etc.

In an embodiment, the undesired vegetation may include *Hibiscus trionum*, *Lolium perenne* L. ssp. *multiflorum* (Lam.) Husnot, *Sida rhombifolia* L., *Anoda cristata* (L.) Schlecht., *Lamium* spp. L., *Cyperus difformis* L., *Croton sperrisfeorus*, *Nicandra physalodes*, *Chenopodium album* L., *Echinochloa colona*, *Amaranthus viridis*, *Hordeum murinum* subsp. *Leporinum*, *Sisymbrium orientate*, *Ipomoea plebeia*, *Cerastium vulgatum*, *Bifora radians* Bieb., *Echinochloa crus-galli* (L.) Beauv., *Digera* spp., *Digera arvensis*, *Arctotheca calendula* (L.) Levyns., *Cynodon dactylone*, *Commelina benghalensis* L., *Eragrostis pilosa* (L.) Beauv., *Amaranthus retroflexus* L., *Amaranthus* sp., *Euphorbia hirta* L., *Datura wrightii* Regel, *Capsella bursa-pastoris* (L.) Medik., *Emex australis*, *Urtica dioica* L., *Veronica hederifolia* L., *Erodium cicutarium*, *Juncus tenuis* Willd., *Juncus bufonius*, *Lythrum hyssopifolia*, *Rapistrum rugosum* (L.) AIL, *Salvia reflexa*, *Buglossoides arvensis* syn *Lithospermum arvens*, *Xanthium pungens*, *Ribes divaricatum*, *Cyperus rotundus*, *Raphanus raphanistrum* L., *Echium*

plantagineum, *Polygonum aviculare* and *Polygonum arenastrum*, *Parthenium*, *Lactuca serriola* L., *Acanthospermum*, *Galium tricornutum* **Dandy**, *Amsinckia calycina* (**Moris**) **Chater**, *Amsinckia intermedia* **Fischer & C. Meyer**, *Amsinckia lycopsoides* (**Lehm.**) **Lehm.**, *Triticum* sp., *Hordeum vulgare*, *Alopecurus myosuroides* **Huds.**, *Lolium* sp.,
 5 *Elymus repens*, *Bromus sterilis*, *Xanthium Spinosum*, *Datura ferox*, *Dinebra Arabica*, *Eleusine indica*, *Cynodon dactylon*, *Euphorbia Hirta*, *Trianthema Portulacasturm*, *Amaranthus deflexus*, *Amaranthus hybridus* L., *Polygonum*, *Persicaria maculosa*, *Synapis arvensis*, *Abutilon theophrasti* **Medik.**, *Ambrosia artemisiifolia* L., *Solanum ptychanthum*, *Xanthium strumarium* L., *Polygonum convolvulus*, *Alopecurus* sp.,
 10 *Bromus madritensis* sp., *Panicum* sp., *Hordeum jubatum* sp., *Setaria* sp., *Panicum capillare* L., *Panicum miliaceum* L., *Digitaria* sp., *Cyperus esculentus* L., *Acanthospermum hispidum* **DC**, *Cynotis* sp., *Tradescantia fluminensis*, *Galinsoga* sp., *Portulaca oleracea* L., *Alternanthera caracasana*, *Tribulus zeyheri*, *Acanthospermum australe*, *Acanthospermum glabratum*, *Cleome monophylla*, *Phyllanthus* sp., *Flaveria*
 15 *bidentis*, *Galinsoga parviflora*, *Soliva sessilis*, *Bidens pilosa*, *Parnassia palustris*, *Eragrostis*, *Ipomeas* sp., *Hierochloa odorata*, *Anthoxanthum nitens*, *Rottboellia cochinchinensis* L., *Schkuhria Bonariensis* L., *Sorghum halepense*, Devil thorn, *Zea mays* L., *Cleome viscosa*, *Parthenium hysterophorus*, *Commelina bengalensis*, *Dinebra* sp., *Portulaca* sp., *Trianthema* sp., *Dactyloctenium aegyptium*, *Corchorus* sp.,
 20 *Trianthema monogyna* and *Brachiaria* sp.

In a specific embodiment, the undesired vegetation may include *Echinochloa Colona*, *Dinebra Arabica*, *Cynotis* sp, *Eleusine Indica*, *Cynodon Dactylon*, *Euphorbia Hirta*, *Amaranthus Viridis*, *Digeria Arvensis*, *Digeria* sp., *Panicum* sp., *Phyllanthus* sp, *Commelina benghalensis* L, *Parthenium*, *Trianthema Portulacasturm*, *Cleome viscosa*,
 25 *Digeria arvensis*, *Parthenium hysterophorus*, *Cynodon dactylone*, *Commelina bengalensis* and *Dinebra* sp., *Portulaca* sp., *Trianthema* sp., *Dactyloctenium aegyptium*, *Corchorus* sp., *Trianthema monogyna*, *Brachiaria* sp.

The described compositions may be made at the time of use, or diluted, or else they can be concentrated compositions, or so-called "ready-to-use" compositions, that is
 30 to say, ready for marketing.

In an embodiment, the formulation may be obtained by combining a synergistic amount of the active ingredients with an agriculturally acceptable carrier, a surfactant or other application-promoting adjuvant customarily employed in formulation technology.

In yet another embodiment, the composition may be employed in any
5 conventional form, for example, in the form of a twin pack, or as emulsion concentrates (EC), microemulsion concentrates (MEC), suspension concentrates (SC), soluble concentrates (SL), suspoemulsion (SE), oil dispersions (OD), water dispersible granules (WDG), water soluble granules (SG) and wettable powders (WP). Such compositions can be formulated using with agriculturally acceptable carriers, surfactants or other
10 application-promoting adjuvants customarily employed in formulation technology and formulation techniques that are known in the art.

In a specific embodiment, the composition of imazethapyr and propaquizafop is an emulsion concentrate, preferably a microemulsion.

In an embodiment, the amount of the mixture of active ingredient in the
15 composition may be about 0.1-99 wt. %, specifically about 0.1-95 wt. %, more specifically about 0.1-90 wt. %, based on the total weight of the composition. In another embodiment, the amount of the mixture of active ingredient in the composition may be about 0.1-50 wt %, specifically about 0.1-25 wt. %, more specifically about 0.1-10 wt. %, based on the total weight of the composition.

20 Examples of suitable liquid carriers to be used in the composition may include water, aromatic hydrocarbons such as alkylbenzenes and alkylnaphthalenes, alcohols such as methanol, cyclohexanol and decanol, ethylene glycol, polypropylene glycol and dipropylene glycol, N,N-dimethylformamide, dimethylsulfoxide, N-alkylpyrrolidone, paraffins, oils of olive, castor, linseed, tung, sesame, corn, peanut,
25 cotton-seed, soybean, rape-seed and coconut, fatty acid esters, ketones such as cyclohexanone, 2-heptanone, isophorone and 4-hydroxy-4-methyl-2-pentanone and the like.

Examples of suitable solid carriers to be used in the composition may include mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk,
30 bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, sodium carbonate and bicarbonate, and sodium sulfate, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium

phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

Examples of suitable surfactants include non-ionic, anionic, cationic and
5 ampholytic types such as alkoxylated fatty alcohols, ethoxylated polysorbate (e.g. tween 20), ethoxylated castor oil, lignin sulfonates, fatty acid sulfonates (e.g. lauryl sulfonate), phosphate esters such as phosphate esters of alcohol alkoxylates, phosphate esters of alkylphenol alkoxylates and phosphate esters of styrylphenol ethoxylates, condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde,
10 condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, alkylarylsulfonates, ethoxylated alkylphenols and aryl phenols, polyalkylene glycols and sorbitol esters.

Other ingredients, such as wetting agents, anti-foaming, adhesives, neutralizers, thickeners, binders, sequestrants, stabilizers, solubilizer, salts, fertilizers or anti-freeze
15 agents, may also be added to the disclosed compositions.

In another embodiment, a kit comprising the herbicidal mixture as described herein, or components thereof, is provided. Such kits may comprise, in addition to the aforementioned active components, one or more additional active and/or inactive ingredients, either within the provided herbicidal composition or separately. Certain kits
20 comprise imazethapyr, propaquizafop, each in a separate container, and each optionally combined with a carrier.

A synergistic effect exists wherever the action of a combination of active components is greater than the sum of the action of each of the components alone. Therefore, a synergistically effective amount (or an effective amount of a synergistic
25 composition or combination) is an amount that exhibits greater pesticidal activity than the sum of the pesticidal activities of the individual components.

In the field of agriculture, it is often understood that the term "synergy" is as defined by Colby S. R. in an article entitled "Calculation of the synergistic and antagonistic responses of herbicide combinations" published in the journal Weeds,
30 1967, 15, p. 20-22, incorporated herein by reference in its entirety. The action expected for a given combination of two active components can be calculated as follows:

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

in which E represents the expected percentage of pesticidal control for the combination of the two pesticides at defined doses (for example equal to x and y respectively), X is the percentage of herbicidal control observed by imazethapyr at a defined dose (equal to x) and Y is the percentage of herbicidal control observed by propaquizafop at a defined dose (equal to y). When the percentage of herbicidal control observed for the combination is greater than the expected percentage, there is a synergistic effect, when the percentage of control observed for the combination is equal to the expected percentage, there is an additive effect and wherein the percentage of herbicidal control observed for the combination is lower than the expected percentage, there is an antagonistic effect.

EXPERIMENTAL DETAILS

Formulation Example

One exemplary embodiment of the ready mix emulsion concentrate formulation is illustrated in Table 1, below:

TABLE 1

Ingredient	% w/w
Propaquizafop	2.86
Imazethapyr	3.95
Surfactants	41.7
Additives	3.64
Solvents	47.85

d= 1.068 g/l.

The above formulation was prepared by forming a mixture comprising 37.5 g of imazethapyr, the surfactants, the additives and dipropylene glycol, propylene glycol and water as solvents. Afterwards, a premix of 25 g of propaquizafop dissolved in Solgad 200 ULN was added to the mixture. This was then stirred until a homogeneous mixture was obtained.

Experiments

The experiments were conducted by tank mixing commercially available Agil (propaquizafop 10% EC, 100 gr/L) and commercially available Weedlock (imazethapyr

10% SL, 100 gr/L) on soybean, black gram, ground nut (peanut), red gram (pigeon peas), green gram, beans, field peas and cluster beans (tables 2-10) in different application rates.

Applications were made with a Knapsack sprayer fitted with Flat fan nozzle for the application of herbicides. Experiment design was in random blocks with three replication and nine treatments.

Species wise weed count recorded at 15 and 30 DAA (Days After Application) by using 0.25 m² quadrant treatment wise in minimum 3 places randomly selected in the plot / replication. The average of each variable was used together with the sum of all the variables per plot to calculate the percentage of control.

The % control observed was calculated as follows:

% control observed =

$$\frac{\text{Mean weed count in untreated control} - \text{Mean weed count in treated plot}}{\text{Mean weed count in untreated control}} * 100$$

15

EXAMPLE 1: Tank mix of Propaquizafop + Imazethapyr on Soybean

TABLE 2

Tank mix of Propaquizafop + Imazethapyr on Soybean							
AI	Application rate (ml/Acre)	% control observed		% control expected		Colby Ratio o/e	
		15DAA	30DAA	15DAA	30DAA	15DAA	30DAA
Propaquizafop	200	64.02	67.08				
Propaquizafop	250	67.78	74.58				
Imazethapyr	300	65.69	66.67				
Imazethapyr	350	66.53	66.25				
Propaquizafop + Imazethapyr	200+300	95.40	98.33	87.65	89.03	1.09	1.10
Propaquizafop + Imazethapyr	200+350	96.65	98.33	87.96	88.89	1.10	1.11
Propaquizafop + Imazethapyr	250+300	93.72	91.25	88.95	91.53	1.05	1.00
Propaquizafop + Imazethapyr	250+350	92.05	92.50	89.22	91.42	1.03	1.01

* DAA means days after treatment.

The trial detailed in Table 2 was conducted on Soybean crop in the district of Singauda, Madhya Pradesh (India). The sowing was done during first week of July with a variety JS9560. Phenological Status: Vegetative growth 20 DAS, Design & Plot size: RBD & 36 Sq.mt. The weeds that have been controlled include *Dinebra*, *Echinochloa colona*, *Eleusine indica*, *Cynodon dactylone*, *Cynotis sp*, *Commelina bengalensis*, *Alternanthera*, and *Parthenium*.

10 EXAMPLE 2: Tank mix of Propaquizafop + Imazethapyr on Black Gram

TABLE 3

Tank mix of Propaquizafop + Imazethapyr on Black gram							
		% control observed		% control expected		Colby Ratio o/e	
AI	Application rate (ml/Acre)	15 DAA	30 DAA	15 DAA	30 DAA	15 DAA	30 DAA
Propaquizafop	200	66.06	70.67				
Propaquizafop	250	68.33	69.33				
Imazethapyr	300	67.87	70.22				
Imazethapyr	350	67.42	64.00				
Propaquizafop + Imazethapyr	200+300	94.12	98.22	89.10	91.27	1.06	1.08
Propaquizafop + Imazethapyr	200+350	96.38	97.33	88.94	89.44	1.08	1.09
Propaquizafop + Imazethapyr	250+300	93.67	94.67	89.83	90.87	1.04	1.04
Propaquizafop + Imazethapyr	250+350	95.02	96.00	89.68	88.96	1.06	1.08

* DAA means days after treatment..

The trial detailed in Table 3 was conducted on Black gram in the district of Kaza, Guntur (Andhra Pradesh, India). The sowing was done during second week of July with a variety LBG756. Phenological Status: Vegetative growth 20 DAS, Design & Plot size: RBD & 20 Sq.mt. The weeds that have been controlled include *Echinochloa colona*, *Panicum sp*, *Amaranthus sp*. and *Phyllanthus sp*.

EXAMPLE 3: Tank mix of Propaquizafop + Imazethapyr on Ground nut (Peanut)

TABLE 4

Tank mix of Propaquizafop + Imazethapyr on ground nut							
		% control observed		% control expected		Colby Ratio o/e	
AI	Application rate (ml/Acre)	15DAA	30DAA	15DAA	30DAA	15DAA	30DAA
Propaquizafop	200	65.07	68.52				
Propaquizafop	250	66.03	69.44				
Imazethapyr	300	68.90	69.44				
Imazethapyr	350	63.64	62.50				
Propaquizafop + Imazethapyr	200+300	96.65	98.15	89.14	90.38	1.08	1.09
Propaquizafop + Imazethapyr	200+350	94.74	97.22	87.30	88.19	1.09	1.10
Propaquizafop + Imazethapyr	250+300	92.82	93.98	89.44	90.66	1.04	1.04
Propaquizafop + Imazethapyr	250+350	94.26	95.83	87.65	88.54	1.08	1.08

* DAA means days after treatment.

- 5 The trial detailed in Table 4 was conducted on Peanut in the district of Koppaka, West Godavari (Andhra Pradesh, India). The sowing was done during second week of August with a variety K20. Phenological Status: Vegetative growth 20 DAS, Design & Plot size: RBD & 20 Sq.mt. The weeds that have been controlled include *Echinochloa colona*, *Trianthema portulacastrum*, *Cleome viscosa*, *Digera arvensis*, and *Parthenium*
- 10 *hysterophorus*.

EXAMPLE 4: Tank mix of Propaquizafop + Imazethapyr on Pigeon peas (Red Gram)

TABLE 5

Tank mix of Propaquizafop + Imazethapyr on Red Gram							
		% control observed		% control expected		Colby Ratio o/e	
AI	Application rate (ml/Acre)	15DAA	30DAA	15DAA	30DAA	15DAA	30DAA
Propaquizafop	200	59.69	65.98				
Propaquizafop	250	63.35	65.98				
Imazethapyr	300	68.59	67.01				
Imazethapyr	350	68.59	59.80				
Propaquizafop + Imazethapyr	200+300	95.29	97.94	87.34	88.78	1.09	1.10
Propaquizafop + Imazethapyr	200+350	96.34	96.91	87.34	86.32	1.10	1.12
Propaquizafop + Imazethapyr	250+300	92.15	94.33	88.49	88.78	1.04	1.06
Propaquizafop + Imazethapyr	250+350	93.72	93.30	88.49	86.32	1.06	1.08

* DAA means days after treatment..

- 5 The trial detailed in Table 5 was conducted on Red gram in the district of Amaravati (Maharashtra, India). The sowing was done during third week of October with a variety Maruti. Phenological Status: Vegetative growth 20 DAS, Design & Plot size: RBD & 30 Sq.mt. The weeds that have been controlled include *Echinochloa colona*, *Panicum sp*, *Amaranthus sp* and *Phyllanthus sp*.

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EXAMPLE 5: Tank mix of Propaquizafop + Imazethapyr on Green gram

TABLE 6

Tank mix of Propaquizafop + Imazethapyr on Green Gram							
		% control observed		% control expected		Colby Ratio o/e	
AI	Application rate (ml/Acre)	15DAA	30DAA	15DAA	30DAA	15DAA	30DAA

Propaquizafop	200	70.98	70.00				
Propaquizafop	250	68.30	72.27				
Imazethapyr	300	67.41	68.18				
Imazethapyr	350	64.29	65.45				
Propaquizafop + Imazethapyr	200+300	94.64	98.18	90.54	90.45	1.05	1.09
Propaquizafop + Imazethapyr	200+350	94.64	98.18	89.64	89.64	1.06	1.10
Propaquizafop + Imazethapyr	250+300	93.30	95.45	89.67	91.18	1.04	1.05
Propaquizafop + Imazethapyr	250+350	92.86	95.45	88.68	90.42	1.05	1.06

* DAA means days after treatment.

The trial detailed in Table 6 was conducted on Green gram in the district of Mogalauru, Krishna (Andhra Pradesh, India). The sowing was done during first week of July with a local variety. Phenological status: vegetative growth 20 DAS. Design & Plot size: RBD & 20 Sq.mt. The weeds that have been controlled include *Echinochloa colona*, *Panicum sp*, *Amaranthus sp* and *Phyllanthus sp*.

EXAMPLE 6: Tank mix of Propaquizafop + Imazethapyr on Ground nut (Peanut)

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TABLE 7

Tank mix of Propaquizafop + Imazethapyr on Ground nut							
		% control observed		% control expected		Colby Ratio o/e	
AI	Application rate (ml/Acre)	15DAA	30DAA	15DAA	30DAA	15DAA	30DAA
Propaquizafop	200	54.07	61.96				
Propaquizafop	250	58.14	65.76				
Imazethapyr	300	56.40	62.50				
Imazethapyr	350	54.65	61.96				
Propaquizafop + Imazethapyr	200+300	93.60	97.83	79.97	85.73	1.17	1.14
Propaquizafop + Imazethapyr	200+350	94.77	97.83	79.17	85.53	1.20	1.14
Propaquizafop + Imazethapyr	250+300	89.53	92.39	81.75	87.16	1.10	1.06

Propaquizafop + Imazethapyr	250+350	90.12	92.93	81.02	86.97	1.11	1.07
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* DAA means days after treatment.

The trial detailed in Table 7 was conducted on Peanut in the district of Koppaka, West Godavari (Andhra Pradesh, India). The sowing was done during second week of August with a variety K20. Phenological Status: Vegetative growth 24 DAS, Design & Plot size: RBD & 20 Sq.mt. The weeds that have been controlled include *Echinochloa colona*, *Brachiaria sp.*, *Digera sp.*, and *Trianthema sp.*

EXAMPLE 7: Tank mix of Propaquizafop + Imazethapyr on Beans

TABLE 8

Tank mix of Propaquizafop + Imazethapyr on Beans							
		% control observed		% control expected		Colby Ratio o/e	
AI	Application rate (ml/Acre)	15DAA	30DAA	15DAA	30DAA	15DAA	30DAA
Propaquizafop	200	61.86	68.87				
Propaquizafop	250	60.82	68.40				
Imazethapyr	300	59.28	69.81				
Imazethapyr	350	58.25	67.92				
Propaquizafop + Imazethapyr	200+300	91.75	98.11	84.47	90.60	1.09	1.08
Propaquizafop + Imazethapyr	200+350	92.27	98.11	84.07	90.01	1.10	1.09
Propaquizafop + Imazethapyr	250+300	87.63	94.34	84.05	90.46	1.04	1.04
Propaquizafop + Imazethapyr	250+350	87.63	94.34	83.64	89.86	1.05	1.05

10 * DAA means days after treatment.

The trial detailed in Table 8 was conducted on beans in the district of Jabalpur, Madhya Pradesh, INDIA. The sowing was done during second week of July with a variety JDL 79 of beans. Phenological Status: Vegetative growth 27 DAS, Design & Plot size: RBD & 20 Sq.mt. The weeds that have been controlled include *Echinochloa colona*, *Panicum sp.*, *Dinebra sp.*, *Portulaca sp.*, *Digera sp.*, and *Trianthema sp.*

EXAMPLE 8: Tank mix of Propaquizafop + Imazethapyr on Field Peas

TABLE 9

Tank mix of Propaquizafop + Imazethapyr on Field Peas							
		% control observed		% control expected		Colby Ratio o/e	
AI	Application rate (ml/Acre)	15DAA	30DAA	15DAA	30DAA	15DAA	30DAA
Propaquizafop	200	61.29	69.15				
Propaquizafop	250	61.83	68.66				
Imazethapyr	300	63.44	70.65				
Imazethapyr	350	60.75	66.17				
Propaquizafop + Imazethapyr	200+300	91.94	98.01	85.85	90.95	1.07	1.08
Propaquizafop + Imazethapyr	200+350	91.40	97.01	84.81	89.56	1.08	1.08
Propaquizafop + Imazethapyr	250+300	88.71	95.52	86.04	90.80	1.03	1.05
Propaquizafop + Imazethapyr	250+350	88.71	95.02	85.02	89.40	1.04	1.06

* DAA means days after treatment..

- 5 The trial detailed in Table 9 was conducted on field peas in the district of Amaravati, Maharashtra, India. The sowing was done during third week of October with a variety of field peas. Phenological Status: Vegetative growth 28 DAS, Design & Plot size: RBD & 20 Sq.mt. The weeds that have been controlled include *Eleusine indica*, *Dactyloctenium aegyptium*, *Corchorus sp.*, and *Trianthema monogyna*.

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EXAMPLE 9: Tank mix of Propaquizafop + Imazethapyr on Cluster Beans

TABLE 10

Tank mix of Propaquizafop + Imazethapyr on Cluster Beans							
		% control observed		% control expected		Colby Ratio o/e	
AI	Application rate (ml/Acre)	15DAA	30DAA	15DAA	30DAA	15DAA	30DAA

Propaquizafop	200	65.64	72.43				
Propaquizafop	250	65.13	71.96				
Imazethapyr	300	62.56	68.69				
Imazethapyr	350	58.97	66.36				
Propaquizafop + Imazethapyr	200+300	93.85	98.13	87.14	91.37	1.08	1.07
Propaquizafop + Imazethapyr	200+350	94.36	98.13	85.90	90.72	1.10	1.08
Propaquizafop + Imazethapyr	250+300	90.77	94.39	86.95	91.22	1.04	1.03
Propaquizafop + Imazethapyr	250+350	90.77	94.86	85.69	90.57	1.06	1.05

* DAA means days after treatment.

The trial detailed in Table 10 was conducted on cluster beans in the district of Nagra, Hanumangarh dt, Rajsthan, India. The sowing was done during second week of July with a variety HG-365 of cluster beans. Phenological Status: Vegetative growth 27 DAS, Design & Plot size: RBD & 50 Sq.mt. The weeds that have been controlled include *Echinochloa colona*, *Panicum sp.*, *Dinebra sp.*, *Portulaca sp.*, *Digera sp.*, and *Trianthema sp.*

DISCUSSION

All the above results show that the percentage of herbicidal control observed for the combination is greater than the expected percentage (Colby Ratio o/e). The data shows efficacy of total weeds (grassy+ broad leaf weed) on soybean, black gram, ground nut (peanut), red gram (pigeon peas), green gram, beans, field peas and cluster beans. In spite of what has been reported in the prior art it can be concluded that by combining imazethapyr and propaquizafop, a herbicidal mixture which has a broader spectrum of activity is obtained without crop damage.

All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated herein by reference.

Features of the disclosed embodiments may be combined, rearranged, omitted, etc., within the scope of the present disclosure to produce additional embodiments. Furthermore, certain features may sometimes be used to advantage without a corresponding use of other features.

It is thus apparent that there is provided in accordance with the present disclosure, mixtures, compositions and methods of a herbicidal mixture. Many alternatives, modifications, and variations are enabled by the present disclosure. While specific embodiments have been shown and described in detail to illustrate the application of the principles of the present subject matter, it will be understood that the subject matter may be embodied otherwise without departing from such principles. Accordingly, Applicants intend to embrace all such alternatives, modifications, equivalents, and variations that are within the spirit and scope of the present subject matter.

CLAIMS

1. A herbicidal mixture comprising imazethapyr and propaquizafop, esters, salts and/or combination thereof.
2. The herbicidal mixture of claim 1, wherein the weight ratio of imazethapyr to propaquizafop is from 20:1 to 1:20.
3. The herbicidal mixture of claim 1 or 2, wherein the weight ratio of imazethapyr to propaquizafop is from 5:1 to 1:5.
4. The herbicidal mixture of any one of claims 1 to 3, wherein the compounds are applied jointly or in a succession.
5. The herbicidal mixture of any one of claims 1 to 4, wherein the application rate of the mixture is from 0.1 liter/ha to 10 liter/ha.
6. The herbicidal mixture of claim 5, wherein the application rate of the mixture is 1.25 liter/ha.
7. The herbicidal mixture of any one of claims 1 to 6 wherein the mixture is applied in an amount of 125 g/ha.
8. The herbicidal mixture of claim 7 wherein the amount of imazethapyr is 75 g/ha and the amount of propaquizafop is 50 g/ha.
9. A herbicidal composition comprising a mixture of imazethapyr and propaquizafop, esters, salts and/or combination thereof, and at least one agriculturally acceptable carrier.
10. The herbicidal composition of claim 9, further comprising at least one surfactant, solid diluent, liquid diluent, or a combination thereof.
11. The herbicidal composition of claim 9 or 10, wherein the composition is a microemulsion.
12. The herbicidal composition of any one of claims 9-11, wherein the weight ratio of imazethapyr to propaquizafop is from 20:1 to 1:20.
13. The herbicidal composition of any one of claims 9-12, wherein the weight ratio of imazethapyr to propaquizafop is from 5:1 to 1:5.
14. The herbicidal composition of any one of claims 9-11, wherein imazethapyr is present in an amount ranging from about 1% -10% w/w based on the total weight of the emulsion concentrate.

15. The herbicidal composition of any one of claims 9-14 wherein propaquizafop is present in an amount ranging from about 1% -10% w/w based on the total weight of the emulsion concentrate.
16. The herbicidal composition of any one of claims 9-15, wherein said acceptable carrier is present in an amount ranging from about 40% -55% w/w based on the total weight of the emulsion concentrate.
17. The herbicidal composition of any one of claims 10-16, wherein said surfactants are present in an amount ranging from about 30% -50% w/w based on the total weight of the emulsion concentrate.
18. A method of controlling undesired vegetation comprising applying to the locus of the undesired vegetation a herbicidally effective amount of a mixture comprising imazethapyr, propaquizafop esters, salts and/or combination thereof.
19. The method of claim 18 wherein the crop is selected from the group consisting of soybeans, blackgram, peanuts, green gram, pigeon pea, beans, field peas and cluster beans.
20. The method of claim 18 or 19, wherein the mixture is applied in an amount of 1 to 500 g/ha.
21. The method of claim 20, wherein the mixture is applied in an amount of 125 g/ha.
22. The method of any one of claims 18-21 wherein the undesired vegetation is selected from the group consisting of *Echinochloa Colona*, *Dinebra Arabica*, *Cynotis sp.*, *Eleusine Indica*, *Cynodon Dactylon*, *Euphorbia Hirta*, *Amaranthus Viridis*, *Digera Arvensis*, *Digera sp.*, *Panicum sp.*, *Phyllanthus sp.*, *Commelina benghalensis L.*, *Parthenium*, *Trianthema Portulacasturm*, *Cleome viscosa*, *Digera arvensis*, *Parthenium hysterophorus*, *Cynadon dactylone*, *Commelina bengalensis* and *Dinebra sp.*, *Portulaca sp.*, *Trianthima sp.*, *Dactyloctenium aegyptium*, *Corchprus sp.*, *Trianthema monogyna*, *Brachiaria sp.*
23. A method of controlling undesired vegetation comprising applying to the locus of the undesired vegetation the composition of any one of claims 9-17.
24. A synergistic herbicidal mixture comprising imazethapyr and propaquizafop, esters, salts and/or combination thereof.

25. The synergistic herbicidal mixture of claim 24, wherein the weight ratio of imazethapyr to propaquizafop is from 20:1 to 1:20.
26. The synergistic herbicidal mixture of claim 24 or 25, wherein the weight ratio of imazethapyr to propaquizafop is from 5:1 to 1:5.
27. The synergistic herbicidal mixture of any one of claims 24 to 26, wherein the compounds are applied jointly or in a succession.
28. The synergistic herbicidal mixture of any one of claims 24 to 27, wherein the application rate of the mixture is from 0.1 liter/ha to 10 liter/ha.
29. The synergistic herbicidal mixture of claim 28, wherein the application rate of the mixture is 1.25 liter/ha.
30. The synergistic herbicidal mixture of any one of claims 24 to 29 wherein the mixture is applied in an amount of 125 g/ha.
31. The synergistic herbicidal mixture of claim 30 wherein the amount of imazethapyr is 75 g/ha and the amount of propaquizafop is 50 g/ha.
32. A kit comprising the herbicidal mixture of claim 1 or claim 24.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2014/061291

A. CLASSIFICATION OF SUBJECT MATTER INV. A01N43/50 A01N43/60 A01P13/00 ADD.		
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) EPO-Internal , WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 482 491 A2 (HOECHST AG [DE]) 29 April 1992 (1992-04-29) page 2, line 3 - page 3, line 4 tables 1, 2	1-32
A	----- WO 98/24321 A1 (CIBA GEIGY AG [CH]) 11 June 1998 (1998-06-11) page 8, paragraph 2 - page 11, paragraph 3 Biological examples; page 19 - page 21 ----- -/--	1-32
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report	
30 July 2014	08/08/2014	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Zanobi ni , Al essandra	

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2014/061291

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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