(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 April 2023 (13.04.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/058032 A1

(51) International Patent Classification:
A01N 37/40 (2006.01) *A01N 43/54* (2006.01)
A01N 39/02 (2006.01) *A01P 13/02* (2006.01)
A01N 39/04 (2006.01) *A01N 25/02* (2006.01)
A01N 43/40 (2006.01)

(21) International Application Number:
PCT/IL2022/051072

(22) International Filing Date:
07 October 2022 (07.10.2022)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
202111045874 08 October 2021 (08.10.2021) IN

(71) Applicant: **ADAMA AGAN LTD.** [IL/IL]; P.O. Box 262, Northern Industrial Zone, 7710201 Ashdod (IL).

(72) Inventors: **SUGATA, Roy**; 70 Elite towers, 16 Jabotinsky Street, 5211401 Ramat Gan (IL). **VENKATESWARARAO, Yadagani**; Plot No: 15, Flat-G1, Sairam Enclave, Saikeerthi Layout, Pragathi Nagar, Hyderabad, Telangana 500090 (IN). **ARUNAGIRINATHAN MANICKAM, Adhimoolam**; 1/3, 20th Cross street, Venkateswara Nagar, Ramapuram, Chennai, Tamil Nadu 600089 (IN).

(74) Agent: **EHRLICH, Gal** et al.; G. E. EHRLICH (1995) LTD., 35, HaMasger Street, 13th Floor, Sky Tower, 6721407 Tel Aviv (IL).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

WO 2023/058032 A1

(54) Title: NOVEL FORMULATION SYSTEMS OF CARBOXYLIC ACID HERBICIDES

(57) Abstract: The present invention relates to a stable and an efficient herbicide formulation system comprising one or more Carboxylic acid herbicides; a metal- chelating agent complex; and a cationic surfactant containing quaternary ammonium moiety, wherein the formulation system helps in interdigitating hydrophobic portion of one or more actives in the surfactant palisade, thereby enhancing efficiency in controlling undesired vegetation.

NOVEL FORMULATION SYSTEMS OF CARBOXYLIC ACID HERBICIDES

RELATED APPLICATION

This application claims benefit of the Indian Provisional Application, IN 202111045874 filed on October 08, 2021; the entire content of which is hereby incorporated by reference herein. Disclosures of the documents and publications referred to herein are hereby incorporated in their entireties by references into this application.

FIELD OF INVENTION

The present invention relates to a stable and an efficient herbicide formulation system comprising one or more Carboxylic acid herbicides; a metal- chelating agent complex; and a cationic surfactant containing quaternary ammonium moiety; and to methods for controlling undesired plant species while leaving the desired species relatively unaffected, by forming an oligomeric surfactant complex which may engulf one or more active compounds, resulting in interdigitating hydrophobic portion of one or more actives in the hydrophobic region of the surfactant palisade, thereby enhancing efficiency.

BACKGROUND OF INVENTION

There are a variety of Carboxylic acid herbicides that are well-known for the selective control of grassy and broadleaf weeds growing in a variety of crops. The use of most of these herbicides are fraught with concerns in recent years as to their safety to human lives and to the environment in general. With respect to post-emergent control of broadleaf and grassy weeds including perennial species, Carboxylic acid herbicides are commonly used. There are quite a few Carboxylic acid herbicide actives available in the art, including 2,4-D (2,4-Dichlorophenoxyacetic acid), Bispyribac (2,6-Bis((4,6-dimethoxypyrimidin-2-yl)oxy) benzoic acid), MCPA (2-methyl-4-chlorophenoxyacetic acid), Dicamba (3,6-dichloro-2-methoxybenzoic acid), MCPP (2-(2-Methyl-4-chlorophenoxy) propanoic acid), Dichlorprop (2-(2,4-Dichlorophenoxy)propanoic acid), Triclopyr (2-(3,5,6-trichloropyridin-2-yl)oxyacetic acid), 2,4,5-T (2,4,5-Trichlorophenoxyacetic acid); Fenoprop (2-(2,4,5-trichlorophenoxy)propionic acid) and agriculturally acceptable salts thereof.

Despite the benefits derived from the use of herbicides in agriculture such as protection of crops and improved productivity, it is always desirable to make judicious spreading and application of herbicide formulations in the fields for its efficient use and to minimize potential health risks associated with an intensive use of agrochemicals.

The vulnerability of crops to undesired vegetation makes weed control one of the major management components of the total crop production system. Undesired broadleaf and grassy weeds including perennial species, are very destructive to crop plants and can significantly reduce crop yields and quality. Selective herbicides help minimize this damage by controlling various undesired weeds.

A typical limitation with water soluble herbicides like Carboxylic acid herbicides is their slow speed of activity. Sometimes herbicidal activity is not seen for several weeks after application. Moreover, the products that are available for use often do not result in adequate weed control with one application, resulting in the need for additional applications in order to achieve acceptable weed control.

There is always a need of an efficient herbicide formulation system which typically broaden spectrum of control, to minimize the doses of chemicals used, to retard resistance development and to reduce the cost of the treatment. Although many formulations of Carboxylic acid herbicides have been studied, the challenge remains to prepare a stable and efficient herbicide formulation system of one or more Carboxylic acid herbicides which provide passage for effective transportation of actives. In the absence of efficient transportation of actives in the formulation, the application of formulation is said to be not well pronounced.

There have been lot of endeavors in the relevant art to prepare effective formulations of Carboxylic acid herbicides. Various surfactant systems were attempted to improve the efficiency of the formulation system of those herbicides. For example, a drag reduction system or spray droplet retention system was achieved in the formulation by mixing cationic surfactant containing quaternary ammonium moiety with 2,4-D. In some other art, metal-chelating agent complex is used along with a carboxylic acid herbicide as an enhancing agent.

However, no prior art has ever addressed the problem in the formulation of insufficient distribution of water soluble herbicide actives, such as 2,4-D and Bispyribac, on the target surface of plant, which is key to the efficiency of formulation regarding both efficacy as well as stability. The meticulous choice of suitable co-formulants and the surfactant system in the formulation may result in surprising outcome to the efficiency of the said formulation.

In light of the above, there is endeavor in the present invention for a novel stable and an efficient herbicide formulation system comprising one or more Carboxylic acid herbicides; and a suitable surfactant system, for increasing the desirable bioavailability and better penetration on the target surface of plant, thereby enhancing overall efficiency of the formulation.

SUMMARY OF THE PRESENT SUBJECT MATTER

We have reasonably addressed the challenges as described above as a whole or in part by arriving at a novel stable herbicide formulation system with suitable coformulants and an inventive surfactant system therein, as defined below.

The present invention relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal-chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety.

The present invention further relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal-chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers.

The present invention relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal-chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; wherein the component (c) is added to a formulation comprising the said components (a) and (b) in effective amounts.

The present invention further relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal-chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers, wherein the component (c) is added to a formulation comprising the said components (a), (b), (d) and (e) in effective amounts.

The present invention also relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides selected from a group consisting of 2,4-D, Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; (b) an effective amount of a metal- chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety.

The present invention also relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides selected from a group consisting of 2,4-D, Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; (b) an effective amount of a metal- chelating agent complex;

(c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers.

The present invention further relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides selected from a group consisting of 2,4-D, Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; (b) an effective amount of a metal- chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety, wherein if two herbicide actives are present in the formulation system, their ratio is in the ranges of 1:50 to 50:1.

The present invention further relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides selected from a group consisting of 2,4-D, Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; (b) an effective amount of a metal- chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers, wherein if two herbicide actives are present in the formulation system, their ratio is in the ranges of 1:50 to 50:1.

The present invention relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides selected from a group consisting of Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; and an effective amount of 2,4-D or its agriculturally acceptable salts; (b) an effective amount of a metal- chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety.

The present invention relates to a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides selected from a group consisting of Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; and an effective amount of 2,4-D or its agriculturally acceptable salts; (b) an effective amount of a metal- chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers.

The present invention further relates to a stable herbicide formulation system comprising (a) an effective amount of 2,4-D or its agriculturally acceptable salt, either alone or in combination with one or more Carboxylic acid herbicides selected from a group consisting of Bispyribac, MCPA,

Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; (b) an effective amount of a metal- chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety.

The present invention further relates to a stable herbicide formulation system comprising (a) an effective amount of 2,4-D or its agriculturally acceptable salt, either alone or in combination with one or more Carboxylic acid herbicides selected from a group consisting of Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; (b) an effective amount of a metal- chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers.

The present invention further specifically relates to a stable herbicide formulation system comprising (a) an effective amount of 2,4-D or its agriculturally acceptable salt, either alone or in combination with Bispyribac, or agriculturally acceptable salts thereof; (b) an effective amount of a metal-aminopolycarboxylate chelating agent complex; and (c) an effective amount of a ethoxylated quaternary ammonium surfactant.

The present invention further specifically relates to a stable herbicide formulation system comprising (a) an effective amount of 2,4-D or its agriculturally acceptable salt, either alone or in combination with Bispyribac, or agriculturally acceptable salts thereof; (b) an effective amount of a metal-aminopolycarboxylate chelating agent complex; (c) an effective amount of a ethoxylated quaternary ammonium surfactant; (d) an effective amount of an alkali metal salt as a pH modifier; and (e) an effective amount of agriculturally acceptable carriers selected from a wetting agent and fillers.

The present invention also provides a method of treating a plant against undesired vegetation comprising applying herbicide formulation system disclosed herein, after dilution with water, to the target sites of the field, so as to treat the plant against undesired vegetation.

The present invention further provides use of the herbicide formulation system disclosed herein for controlling grassy and broadleaf weeds such as Echinochloa spp., Cyperus spp., Ammania spp., Phyllanthus niruri, Digitaria spp., Dactyloctenium spp., Alternenthera sessilis, Commelina communis, Eclipta alba., and Ludvigia spp. on Rice fields.

The present invention also provides a process for the preparation of the herbicide formulation system disclosed herein from individual component parts.

The present invention further provides a method of controlling undesired vegetation comprising applying to the locus the herbicide formulation system disclosed herein. The present

invention also provides a method for controlling grassy and broadleaf weeds comprising diluting with water herbicide formulation system disclosed herein, and applying the aqueous formulation to the locus of the plant.

The present invention provides a method of controlling undesired vegetation comprising applying to the locus the herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal- chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; wherein the component (c) is added to a formulation comprising the said components (a) and (b), wherein the component (c) and the said formulation exist in a ratio ranging from 1:1 to 1:10.

The present invention also provides a method of controlling undesired vegetation comprising applying to the locus the herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal- chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers, wherein the component (c) is added to a formulation comprising the said components (a), (b), (d) and (e), wherein the component (c) and the said formulation exist in a ratio ranging from 1:1 to 1:10.

DETAILED DESCRIPTION OF THE PRESENT SUBJECT MATTER

Definitions

Prior to setting forth the present subject matter in detail, it may be helpful to provide definitions of certain terms to be used herein. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this subject matter pertains.

Certain exemplary embodiments are described to provide an overall understanding of the principles of the invention disclosed herein. It is assumed that those skilled in the art will understand that the inventive features and methods specifically described herein and illustrated in the experimental section are non-limiting exemplary embodiments and that the scope of the present invention is defined solely by the claims. The features illustrated or described in one exemplary embodiment may be combined with the features of other embodiments. Such modifications and variations are intended to be included within the scope of the present invention.

Reference will now be made in detail to embodiments, which are illustrated in the subsequent paragraphs, wherein reference numerals refer to like elements throughout. In this regard, the present embodiments may have different forms and should not be construed as being limited to the

descriptions set forth herein. Accordingly, the embodiments are merely described below to explain aspects of the present disclosure.

As used herein, the term "pesticide" in general broadly refers to an agent that can be used to control and/or kill a pest. The term is understood to include but is not limited to fungicides, insecticides, nematicides, herbicides, acaricides, parasiticides or other control agents. For chemical classes and applications, as well as specific compounds of each class, see "The Pesticide Manual Thirteenth Edition" (British Crop Protection Council, Hampshire, UK, 2003), as well as "The e-Pesticide Manual, Version 3" (British Crop Protection Council, Hampshire, UK, 2003-04), the contents of each of which are incorporated herein by reference in their entirety.

As used herein, the term “system” means but is not limited to an assemblage of active ingredients and/or acceptable coformulants for application either by simultaneous, contemporaneous and/or succession application. It also means a combination in any time of application of the individual components e.g. succession and/or in any physical form, e.g. blend, solution, suspension, dispersion, emulsion, alloy, or the like. “System” also may refer to combining and applying the active components and acceptable coformulants as one composition and/or formulating each of the active component in the mixture or combination as separated compositions and application at the same time or in separated applications at the same time or different times.

The admixture or individual components may be in any physical form, e.g. blend, solution, suspension, dispersion, emulsion, alloy, or the like.

As used herein, the term “agrochemically effective amount” refers to an amount of the active component that is commercially recommended for use to control weed. The commercially recommended amount for each active component, often specified as application rates of the commercial formulation, may be found on the label accompanying the commercial formulation. The commercially recommended application rates of the commercial formulation may vary depending on factors such as the plant species and the weeds to be controlled.

As used herein, the term “more effective” includes, but is not limited to, increasing efficacy of weed control, prolonging protection and reducing the amount of time needed to achieve a given level of weed control, prolonging the duration of protection against weeds after application and extending the protection period against weeds and/or reducing the amount of time needed to achieve a level of weed control compared to the herbicide formulation without suitable coformulants therein.

As used herein, the term “effective” when used in connection with any mixture or formulation system may be but is not limited to increase in controlling weeds, decrease time for effective controlling weeds, decrease the amount of the herbicide(s) which is required for effective controlling

weed, extend the controlling effect of the individual herbicide active in the mixture in terms of type of crop and weed, prolong the time of controlling effect of the formulation. In particular, the term “effective” may refer to, increasing efficacy of weed control in untreated plant area, reducing the amount of time needed to achieve a given level of weed control, extending the protection period against weed and/or reducing the amount of time needed to achieve a level of weed control.

As used herein, the term "effective amount" refers to an amount of the individual components in an agrochemical formulation system or of the mixture which is critical for manufacturing effective formulation as well as for controlling harmful weed on crop plants and does not cause any significant damage to the treated crop plants.

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

As used herein, the term “coformulants” is defined as any substance that itself is not an active ingredient but is added to the composition or formulation such as additives, thickening agent, sticking agents, wetting agent, surfactants, anti-oxidation agent, anti-foaming agents and thickeners.

As used herein the term "plant" or "crop" includes reference to agricultural crops including field crops (soybean, maize, wheat, rice, etc.), vegetable crops (potatoes, cabbages, etc.), fruits (peach, etc.), semi-perennial crops (sugarcane) and perennial crops (coffee and guava).

As used herein the term "plant" or “crop” includes reference to whole plants, plant organs (e.g. leaves, stems, twigs, roots, trunks, limbs, shoots, fruits etc.), plant cells, seedling or plant seeds. This term also encompasses plant crops such as fruits.

The term “plant” may also include the propagation material thereof, which may include all the generative parts of the plant such as seeds and vegetative plant material such as cuttings and tubers, which can be used for the multiplication of the plant. It may also include spores, corms, bulbs, rhizomes, sprouts, basal shoots, stolons, and buds and other parts of plants, including seedlings and young plants, which are to be transplanted after germination, rooting or after emergence from soil or any other kind of substrate, be it artificial or natural.

As used herein, the term "locus" includes not only areas where weeds may already be shown, but also areas where undesired vegetation have yet to show and also area under cultivation. Locus include but is not limited to soil and other plant growth medium.

As used herein, the terms “control” or “controlling” or "treating" refers but is not limited to preventing weeds, protecting plants from weeds, delaying the onset of undesired vegetation, and combating weeds.

The term "applying" or "application", as used herein, refers but is not limited to applying the compounds and compositions of the invention to the plant, to a site of weeds, to a potential site of weeds, which may require protection from undesired vegetation, or the environment around the habitat or potential habitat of the weeds. The application may be by methods described in the present invention such as by spraying, dipping, etc.

Throughout the application, descriptions of various embodiments the term “comprising” is used; 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.” The term “a” or “an” as used herein includes the singular and the plural, unless specifically stated otherwise. Therefore, the terms “a,” “an”, “one or more” or “at least one” can be used interchangeably in this application.

Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may 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.

In this regard, use of the term “about” herein specifically includes ±10% from the indicated values in the range. In addition, the endpoints of all ranges directed to the same component or property herein are inclusive of the endpoints, are independently combinable, and include all intermediate points and ranges.

As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. Expressions such as "at least one of," when preceding a list of elements, modify the entire list of elements and do not modify the individual elements of the list.

For purposes of better understanding the present teachings and in no way limiting the scope of the teachings, each numerical parameter should be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. In this regard, used of the term "about" herein specifically includes ±10% from the indicated values in the range. In addition, the endpoints of all ranges directed to the same component or property herein are inclusive of the endpoints, are independently combinable, and include all intermediate points and ranges.

Herbicide formulations

There is always a challenge to formulate a herbicide formulation system comprising water soluble herbicide active having a suitable surfactant system, for increasing the desirable

bioavailability and better penetration on the target surface of plant, resulting enhancement of overall efficiency of the formulation.

In this endeavor, the inventors have attempted several options to make a stable and efficient formulation system by judiciously choosing conglomerate of coformulants which may result in creating a conducive environment for the active ingredients to transport and make deposition on the target sites. Several combinations of inert components or coformulants were tried, and eventually the desired results were arrived at.

After several experimentations, it is surprisingly found that the formation of oligomeric surfactant complex resulting from the multivalent binding of ethylenediamine di(hydroxyphenyl acetic) acid with a cationic surfactant containing quaternary ammonium moiety, might result in engulfing one or more active compounds, causing interdigitation of hydrophobic portion of one or more actives in the hydrophobic region of the surfactant palisade, thereby enhancing overall efficiency of the formulation system.

In a specific embodiment, the formation of oligomeric surfactant complex by interaction between a cationic surfactant containing quaternary tallow ammonium ethoxylate chloride and Iron-ethylenediamine di(hydroxyphenyl acetic) acid (FeEDDHA) enable enhances packing of surfactant self-assembly in solution and causing deposition of formulation on the plant surfaces. The compact packing of surfactant in the oligomeric complex facilitate transient leaf surface modulation and provide passage for effective transportation of actives.

The additional significant advantage of this formulation system of the present invention is that the oligomeric complex between cationic surfactant and ethylenediamine di(hydroxyphenyl acetic) acid in the metal-complex facilitates the environment for coordination with iron causing effective absorption of metal micro nutrient.

In an embodiment, the present invention provides a formulation system of carboxylic acid herbicide, wherein multivalent anionic ethylenediamine di(hydroxyphenyl acetic) acid, FeEDDHA binds two to four cationic quaternary tallow ammonium ethoxylate chloride surfactant to form oligomeric complex.

In another embodiment, the present invention provides a formulation system of carboxylic acid herbicide, wherein attraction between anionic ethylenediamine di(hydroxyphenyl acetic) acid and quaternary tallow ammonium ethoxylate chloride surfactant screens electrostatic repulsion between surfactant headgroups and favour compact packing of surfactant assembly at interface.

In another embodiment, the present invention provides a formulation system of carboxylic acid herbicide, wherein Iron- Ethylenediamine di(hydroxyphenyl acetic) acid complex alone or in

combination with carboxylic acid herbicide acts as hydrotrope for cationic surfactant to reduce drag in the formulation during spraying.

In another embodiment, the present invention provides a formulation system of carboxylic acid herbicide, wherein surfactant oligomeric complex in the formulation modulates the environment surrounding the actives thereby resulting in distribution and facilitating availability of actives during deposition by translocation and drying.

In an embodiment, the present invention provides a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal- chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety.

In an embodiment, the present invention provides a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal- chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers.

In an embodiment, the present invention provides a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal- chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; wherein the component (c) is added to a formulation comprising the said components (a) and (b) in effective amounts.

In an embodiment, the present invention provides a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal- chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers, wherein the component (c) is added to a formulation comprising the said components (a), (b), (d) and (e) in effective amounts.

In an embodiment, the present invention provides a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal- chelating agent complex; and (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; wherein the component (c) is added to a formulation comprising the said components (a) and (b) in effective amounts, and the component (c) and the formulation exist in a ratio ranging from 1:1 to 1:10.

In an embodiment, the present invention provides a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides; (b) an effective amount of a metal- chelating agent complex; (c) an effective amount of a cationic surfactant containing quaternary ammonium moiety; (d) an effective amount of a pH modifier; and (e) an effective amount of agriculturally acceptable carriers, wherein the component (c) is added to a formulation comprising the said components (a), (b), (d) and (e) in effective amounts, and the component (c) and the formulation exist in a ratio ranging from 1:1 to 1:10.

In an embodiment, the present invention provides a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides, which are selected from a group consisting of 2,4-D, Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof.

In an embodiment, the present invention provides a stable herbicide formulation system comprising (a) an effective amount of one or more Carboxylic acid herbicides, wherein if two herbicide actives are present in the formulation system, their ratio is in the ranges of 1:50 to 50:1.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the metal- chelating agent complex is present in about 5-30% by weight of the formulation.

In an embodiment, the present invention further provides a stable herbicide formulation system, wherein the pH modifier is present in about 1-10% by weight of the formulation.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the agriculturally acceptable carriers are present in about 20-50% by weight of the formulation.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein herbicide actives comprising (i) an effective amount of one or more Carboxylic acid herbicides selected from a group consisting of Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; and (ii) an effective amount of 2,4-D or its agriculturally acceptable salts.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein herbicide actives comprising (i) an effective amount of Bispyribac or an agriculturally acceptable salt thereof, and (ii) an effective amount of 2,4-D or an agriculturally acceptable salt thereof.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein herbicide actives comprising (i) an effective amount of Bispyribac or its sodium salt, and (ii) an effective amount of 2,4-D or its sodium salt in a weight ratio of about 1:10 to 1:50.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of 2,4-D or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of Bispyribac or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of MCPA or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of Dicamba or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of MCPP or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of Dichlorprop or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of Triclopyr or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of 2,4,5-T or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the formulation system comprising an effective amount of Fenoprop or its agriculturally acceptable salt.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the metal in metal- chelating agent complex is selected from a group comprising Iron, Calcium, Copper, Magnesium, Manganese and Zinc.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the chelating agent in metal- chelating agent complex is selected from a group comprising Amino polycarboxylate and polycarboxylates.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the chelating agent in metal- chelating agent complex is selected from a group comprising Ethylenediaminetetraacetic acid (EDTA), Ethylenediamine triacetic acid, Ethylenediamine diacetic acid, Ethylenediamine disuccinic acid, Ethylenetriaminepentaacetic acid (DTPA), Hydroxyethyl ethylenediamine triacetic acid (HEEDTA), Ethylenediamine di[(2-hydroxy-5-sulfophenyl) acetic acid] (EDDHSA), Ethylenediamine di[(hydroxyphenyl)acetic acid] (EDDHA), Ethylenediamine di[(ortho-hydroxyphenyl)acetic acid] (o,o-EDDHA), Ethylenediamine [(ortho-hydroxyphenyl) acetic acid]-[(para-hydroxyphenyl) acetic acid ([o,p] EDDHA), Ethylenediamine di[(ortho-hydroxy-

methylphenyl)acetic acid] (o,o-EDDHMA), Iminodiacetic acid, Iminodisuccinic acid, oxalic acid, tartaric acid, citric acid, nitrilotriacetic acid, glutamic acid; and polyphosphate, tripolyphosphate, sodium trimetaphosphate; diethylenetriamine methyl phosphonic acid, diethylenetriamine pentakis (methylenephosphonic acid), 1,2-diaminoethane tetrakis (methylenephosphonic acid), nitrilotris (methylenephosphonic acid); phosphono butanetricarboxylic acid.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the metal- chelating agent complex is Iron- ethylenediamine di(hydroxyphenyl acetic) acid complex.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the quaternary ammonium moiety in the cationic surfactant is selected from a group comprising bis(hydroxyethyl)methyltallow alkyl ethoxylated chlorides, octadecylmethyl ethoxylated (2EO) quaternary ammonium, octadecylmethyl ethoxylated (15EO) quaternary ammonium, cocoalkylmethyl ethoxylated (2EO) quaternary ammonium, cocoalkylmethyl ethoxylated (15EO) quaternary ammonium, tallowalkylmethyl ethoxylated (5EO) quaternary ammonium, and tallowalkylmethyl ethoxylated (15EO) quaternary ammonium.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the cationic surfactant is Adsee 611 containing bis(hydroxyethyl)methyltallow alkyl ethoxylated chlorides.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the pH modifier is selected from a group comprising sodium carbonate, sodium bicarbonate, potassium carbonate and potassium bicarbonate.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the pH modifier is sodium carbonate.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein agriculturally acceptable carrier is a wetting agent which is selected from a group comprising Alcohol ethoxylates.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein the wetting agent is Lutensol AT50.

In an embodiment, the present invention provides a stable herbicide formulation system, wherein agriculturally acceptable carrier is a filler which is selected from a group comprising China Clay, Precipitated silica and combination thereof.

In an embodiment, the present invention provides a method of treating a plant against undesired weeds comprising applying herbicide formulation system as discussed herein, after dilution with water, to the target sites of the field, so as to treat the plant against undesired weeds.

In an embodiment, the present invention provides a method of treating a plant against undesired weeds, wherein the undesired weeds are selected from a group comprising grassy and broadleaf weeds.

In an embodiment, the present invention provides a use of the herbicide formulation system as discussed herein, for controlling grassy and broadleaf weeds.

In an embodiment, the present invention provides a use of the herbicide formulation system as discussed herein, wherein grassy and broadleaf weeds are selected from a group comprising Echinochloa spp., Cyperus spp., Ammania spp., Phyllanthus niruri, Digitaria spp., Dactyloctenium spp., Alternenthera sessilis, Commelina communis, Eclipta alba., and Ludvigia spp. on Rice fields.

The following examples illustrate the practice of the present invention in some of its embodiments but should not be construed as limiting the scope of the invention. Other embodiments will be apparent to one skilled in the art from consideration of the specification and examples. It is intended that the specification, including the examples, is considered exemplary only without limiting the scope and spirit of the invention.

PREPARATORY EXAMPLES:

Formulation:

One exemplary embodiment of the formulation* of the present invention is illustrated in the below Table 1:

Table 1

Ingredient	**Function**	**w/w**
2,4-D sodium Salt Monohydrate (@94.5 purity)	Active ingredient	57.46
Bispyribac sodium (@97% purity)	Active ingredient	2
Fe EDDHA	Chelant micronutrient	15
Alcohol ethoxylate (Lutensol AT50)	Wetting agent	5
China Clay	Filler	6
Sodium carbonate anhydrous	pH modifier	1
Precipitated silica	Filler	13.5

* The herbicide formulation system of the present invention is illustrated when the surfactant, ADSEE 611 [bis(hydroxyethyl)methyltallow alkyl ethoxylated chlorides] is tank-mixed with the formulation of Table 1.

The formulation was prepared by following below procedures:

1. All the ingredients in the given proportions in the table is charged into the clean blender and the mixture was pre-blended for 45 minutes.

2. The pre blended materials are ground through a jet mill to reduce the particle size such that when subjected to wet sieve test > 99.9%, particles will pass through 350 BSS sieve.

3. The jet milled material in a ribbon blender is post-blended until a dry homogeneous free flowing powder is obtained.

The formulation system of the present invention is finally prepared in the following manner:

1. 250 ml Adsee 611 is dissolved in 150 liter water and to which 500 g of above formulation is added and mixed well. This formulation system is meant to be sprayed in the field area of 1 acre.

The chemical composition of Adsee 611 (as per MSDS) is as follows:

Chemical Name	CAS-No.	GHS Classification	Concentration[%]
Tallow alkylamine ethoxylate propoxylate	68213-26-3	Acute Tox. 4; H302 Aquatic Acute 1; H400 Aquatic Chronic 1; H410 M-Factor (Acute): 1	>= 50 - < 70
Quaternary ammonium compounds, bis(hydroxyethyl)methyltallow alkyl, ethoxylated, chlorides	64755-05-1	Acute Tox. 5; H303 Skin Irrit. 3; H316 Eye Irrit. 2A; H319 Aquatic Acute 3; H402 Aquatic Chronic 3; H412	>= 30 - < 50
Tallow alkylamine ethoxylate	61791-26-2	Acute Tox. 4; H302 Skin Irrit. 2; H315 Eye Irrit. 2A; H319 Aquatic Acute 1; H400 M-Factor (Acute): 1	>= 0.1 - < 1

The density of Adsee 611 is reported to be 1g/ml.

The formulations as recited in the present invention are only exemplified in the following batches (Batch 01-04):

	Batch-01	**Batch-02**
Ingredient	**w/w**	**w/w**
2,4-D sodium Salt Monohydrate (@94.5% purity)	58.62	58.6
Bispyribac sodium (@97% purity)	2.16	2.1
Fe EDDHA	0	15
Alcohol ethoxylate (Lutensol AT50)	5	5
China Clay	21	6
Sodium carbonate anhydrous	1	1

Precipitated silica	12.22	12.3

* ADSEE 611 is tank-mix surfactant before spraying

	Batch-03
Ingredient	**w/w**
2,4-D sodium Salt Monohydrate (@94.5% purity)	58.62
Bispyribac sodium (@97% purity)	2.16
Fe EDDHA	15
Alcohol ethoxylate (Lutensol AT50)	5
Sucrose	13.22
Sodium carbonate anhydrous	1
Precipitated silica	5

* ADSEE 611 is tank-mix surfactant before spraying

	Batch-04
Ingredient	**w/w**
2,4-D sodium Salt Monohydrate (@94.5% purity)	58.62
Bispyribac sodium (@97% purity)	2.16
Fe EDDHA	15
Alcohol ethoxylate (Lutensol AT50)	5
China Clay	4
Sodium carbonate anhydrous	1
Sodium Tripolyphosphate	2
Precipitated silica	12.22

* ADSEE 611 is tank-mix surfactant before spraying

Note: Batch- 01 does not contain Fe EDDHA (metal- chelating agent complex) which is an essential component of the formulation system of the present invention. Batch- 01 was prepared just to conduct the comparative study of the formulation with the formulation system (i.e. Batch 02-04) of the present invention.

As an exemplary embodiment the physicochemical result of the formulation (Batch-02) at ambient and at 54C after 14 days is as below.

S. No.	Test		Ambient	Ambient 14 Day	54°C,14 Day
1	Appearance		Light to Dark brown powder	Light to Dark brown powder	Light to Dark brown powder
2	Active Content (% by weight)				
	2, 4-D Sodium, %w/w		54.26	54.22	54.18
	Bispyribac sodium, %w/w		2.12	2.14	2.1
3	pH (1% w/v aqueous)		8.55	8.64	8.61
4	Persistent Foam in ml after 1 minute, Max		0 ml	0 ml	0 ml
5	Degree of dissolution and solution stability (0.3 g in 100 ml), residue %w/w, Max	5 min	<0.1ml	<0.1ml	<0.1ml
		18 hour	<0.1ml	<0.1ml	<0.1ml
6	Wet Sieve Test in % w/w retention on 350 BSS, Max		NIL	NIL	NIL
7	Wettability in sec, Max		33 sec	29 sec	25 sec

The field evaluation of formulations having compositions Batch 01-03 are conducted at multiple locations for weed control in paddy. Observations at 30 days after application and 45 days after application for different weeds like Echinochloa spp., Cyperus spp., Ammania spp., Phyllanthus niruri, Digitaria spp., and Dactyloctenium spp. are given in tables below:

Location-01. Crop: Paddy, Observation: 30 Days after application										
S.NO.	Treatment	Dose, g or ml /ha	Phyllanthus niruri		Cyperus spp.		Digitaria spp		Dactyloctenium spp	
			Weed count/m2	% Efficacy	Weed count/m2	% Efficacy	Weed count/m2	% Efficacy	Weed Count/m2	% Efficacy
1	Untreated Control	NA	188	0	36	0	104	0	28	0
2	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@ 0 ml/ha	76	59.57	14.67	59.26	80	23.08	20	28.57
3	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@315ml/ha	60	68.09	12	66.67	72	30.77	17.33	38.1
4	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@625ml/ha	48	74.47	9.33	74.07	56	46.15	16	42.86
5	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@940ml/ha	40	78.72	6.67	81.48	52	50	14.67	47.62
6	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	2500 g/ha + ADSEE 611@1250 ml/ha	32	82.98	5.33	85.19	44	57.69	13.33	52.38
7	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@ 0 ml/ha	44	76.6	12	66.67	68	34.62	17.33	38.1
8	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@315ml/ha	24	87.23	8	77.78	60	42.31	16	42.86
9	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@625ml/ha	16	91.49	4	88.89	52	50	13.33	52.38
10	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@940ml/ha	6.67	96.45	2.67	92.59	44	57.69	12	57.14
11	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	2500 g/ha + ADSEE 611@1250 ml/ha	2.67	98.58	0	100	40	61.54	9.33	66.67
12	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@ 0 ml/ha	48	74.47	13.33	62.96	72	30.77	18.67	33.33
13	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@315ml/ha	28	85.11	9.33	74.07	68	34.62	17.33	38.1
14	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@625ml/ha	24	87.23	5.33	85.19	56	46.15	16	42.86
15	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@940ml/ha	18.67	90.07	4	88.89	48	53.85	14.67	47.62
16	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	2500 g/ha + ADSEE 611@1250 ml/ha	10.67	94.33	1.33	96.3	44	57.69	12	57.14

Location-01. Crop: Paddy, Observation: 45 Days after application										
S.NO.	Treatment	G a.i/ha	Phyllanthus niruri		Cyperus spp.		Digitaria spp		Dactyloctenium spp	
			Weed count/m2	% Efficacy	Weed count/m2	% Efficacy	Weed count/m2	% Efficacy	Weed count/m2	% Efficacy
1	Untreated Control	NA	248	0	41.33	0	116	0	40	0
2	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@ 0 ml/ha	108	56.45	20	51.61	92	20.69	32	20
3	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@315ml/ha	96	61.29	16	61.29	88	24.14	28	30
4	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@625ml/ha	76	69.35	12	70.97	72	37.93	25.33	36.67
5	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@940ml/ha	60	75.81	9.33	77.42	64	44.83	24	40
6	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	2500 g/ha + ADSEE 611@1250 ml/ha	52	79.03	8	80.65	56	51.72	22.67	43.33
7	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@ 0 ml/ha	72	70.97	14.67	64.52	84	27.59	28	30
8	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@315ml/ha	40	83.87	9.33	77.42	72	37.93	25.33	36.67
9	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@625ml/ha	28	88.71	6.67	83.87	68	41.38	24	40
10	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@940ml/ha	16	93.55	4	90.32	60	48.28	20	50
11	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	2500 g/ha + ADSEE 611@1250 ml/ha	12	95.16	2.67	93.55	56	51.72	16	60
12	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@ 0 ml/ha	76	69.35	17.33	58.06	88	24.14	28	30
13	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@315ml/ha	44	82.26	9.33	77.42	84	27.59	26.67	33.33
14	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@625ml/ha	36	85.48	8	80.65	69.33	40.23	25.33	36.67
15	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@940ml/ha	24	90.32	5.33	87.1	60	48.28	24	40
16	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	2500 g/ha + ADSEE 611@1250 ml/ha	20	91.94	4	90.32	56	51.72	21.33	46.67

Location-02. Crop: Paddy, Observation: 30 Days after application						
S.No.	Treatment	Dose (g or ml/ha)	Echinochloa sp.		Ammania sp.	
			Weed count/m2	% Efficacy	Weed count/m2	% Efficacy
1	Untreated Control	NA	80	0	51.67	0
2	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@ 0 ml/ha	37.33	53.33	11	78.71
3	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@315ml/ha	15.67	80.42	9	82.58
4	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@625ml/ha	14	82.5	7.67	85.16
5	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@940ml/ha	10.67	86.67	4.33	91.61
6	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	2500 g/ha + ADSEE 611@1250 ml/ha	2.33	97.08	0.67	98.71
7	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@ 0 ml/ha	33.33	58.33	0.67	98.71
8	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@315ml/ha	11	86.25	0.33	99.35
9	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@625ml/ha	4.67	94.17	0.33	99.35
10	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@940ml/ha	1.67	97.92	0	100
11	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	2500 g/ha + ADSEE 611@1250 ml/ha	0	100	0	100
12	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@ 0 ml/ha	36.67	54.17	3.33	93.55
13	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@315ml/ha	14	82.5	2.33	95.48
14	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@625ml/ha	11.33	85.83	1.67	96.77
15	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@940ml/ha	8.67	89.17	0.67	98.71
16	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	2500 g/ha + ADSEE 611@1250 ml/ha	1.33	98.33	0.33	99.35

Location-03. Crop: Paddy, Observation: 30 Days after application						
S.No.	Treatment	Dose (g or ml/ha)	Cyperus sp.		Echinochloa sp.	
			Weed count/m2	% Efficacy	Weed count/m2	% Efficacy
1	Untreated Control	NA	33.67	0	20	0
2	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@ 0 ml/ha	11.67	65.35	9.33	53.33
3	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@315ml/ha	9.33	72.28	3.92	80.42
4	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@625ml/ha	7	79.21	3.5	82.5
5	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	1250 g/ha + ADSEE 611@940ml/ha	4.67	86.14	2.67	86.67
6	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-01)	2500 g/ha + ADSEE 611@1250 ml/ha	4	88.12	0.58	97.08
7	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@ 0 ml/ha	8.33	75.25	8.33	58.33
8	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@315ml/ha	6	82.18	2.75	86.25
9	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@625ml/ha	2.33	93.07	1.17	94.17
10	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	1250 g/ha + ADSEE 611@940ml/ha	1.33	96.04	0.42	97.92
11	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-02)	2500 g/ha + ADSEE 611@1250 ml/ha	0	100	0	100
12	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@ 0 ml/ha	9	73.27	9.17	54.17
13	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@315ml/ha	6.33	81.19	3.5	82.5
14	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@625ml/ha	3	91.09	2.83	85.83
15	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	1250 g/ha + ADSEE 611@940ml/ha	2.67	92.08	2.17	89.17
16	2, 4-D Sodium 54.3 + Bispyribac sodium 2 SP (Batch-03)	2500 g/ha + ADSEE 611@1250 ml/ha	0	100	0.33	98.33

The formulation system of the present invention containing metal-chelating agent and cationic surfactant exhibited enhanced weed control efficacy compared to the formulations where either of them is absent. Regrowth as well as new germination of broad leaf weeds and grasses were also observed after 30 days after application with the composition that does not contain metal-chelating agent and cationic surfactant.

In addition, any priority document(s) of this application is/are hereby incorporated herein by reference in its/their entirety.

WHAT IS CLAIMED IS:

1. A stable herbicide formulation system comprising:
(a) an effective amount of one or more Carboxylic acid herbicides;
(b) an effective amount of a metal- chelating agent complex; and
(c) an effective amount of a cationic surfactant containing quaternary ammonium moiety;

2. The stable herbicide formulation system of claim 1 further comprising (d) an effective amount of a pH modifier and (e) an effective amount of agriculturally acceptable carriers.

3. The stable herbicide formulation system of claim 1, wherein the component (c) is added to a formulation comprising the said components (a) and (b) in effective amounts.

4. The stable herbicide formulation system of claim 2, wherein the component (c) is added to a formulation comprising the said components (a), (b), (d) and (e) in effective amounts.

5. The stable herbicide formulation system of any one of claims 1-4, wherein the component (c) and the formulation exist in a ratio ranging from 1:1 to 1:10.

6. The stable herbicide formulation system of claim 1, wherein one or more Carboxylic acid herbicides are selected from a group consisting of 2,4-D, Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof.

7. The stable herbicide formulation system of claim 6, wherein if two herbicide actives are present in the formulation system, their ratio is in the ranges of 1:50 to 50:1.

8. The stable herbicide formulation system of any one of claims 1-4, wherein the metal- chelating agent complex is present in about 5-30% by weight of the formulation.

9. The stable herbicide formulation system of claim 2, wherein the pH modifier is present in about 1-10% by weight of the formulation.

10. The stable herbicide formulation system of claim 2, wherein the agriculturally acceptable carriers are present in about 20-50% by weight of the formulation.

11. The stable herbicide formulation system of any one of claims 1-7, wherein herbicide actives comprising (i) an effective amount of one or more Carboxylic acid herbicides selected from a group consisting of Bispyribac, MCPA, Dicamba, MCPP, Dichlorprop, Triclopyr, 2,4,5-T, Fenoprop and agriculturally acceptable salts thereof; and (ii) an effective amount of 2,4-D or its agriculturally acceptable salts.

12. The stable herbicide formulation system of claim 11, wherein herbicide actives comprising (i) an effective amount of Bispyribac or an agriculturally acceptable salt thereof, and (ii) an effective amount of 2,4-D or an agriculturally acceptable salt thereof.

13. The stable herbicide formulation system of claim 12, wherein herbicide actives comprising (i) an effective amount of Bispyribac or its sodium salt, and (ii) an effective amount of 2,4-D or its sodium salt in a weight ratio of about 1:10 to 1:50.

14. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of 2,4-D or its agriculturally acceptable salt.

15. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of Bispyribac or its agriculturally acceptable salt.

16. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of MCPA or its agriculturally acceptable salt.

17. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of Dicamba or its agriculturally acceptable salt.

18. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of MCPP or its agriculturally acceptable salt.

19. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of Dichlorprop or its agriculturally acceptable salt.

20. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of Triclopyr or its agriculturally acceptable salt.

21. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of 2,4,5-T or its agriculturally acceptable salt.

22. The stable herbicide formulation system of any one of claims 1-6, wherein the formulation system comprising an effective amount of Fenoprop or its agriculturally acceptable salt.

23. The stable herbicide formulation system of any one of claims 1-22, wherein the metal in metal-chelating agent complex is selected from a group comprising Iron, Calcium, Copper, Magnesium, Manganese and Zinc.

24. The stable herbicide formulation system of any one of claims 1-22, wherein the chelating agent in metal- chelating agent complex is selected from a group comprising Amino polycarboxylate and polycarboxylates.

25. The stable herbicide formulation system of claim 24, wherein the chelating agent in metal-chelating agent complex is selected from a group comprising Ethylenediaminetetraacetic acid (EDTA), Ethylenediamine triacetic acid, Ethylenediamine diacetic acid, Ethylenediamine disuccinic acid, Ethylenetriaminepentaacetic acid (DTPA), Hydroxyethyl ethylenediamine triacetic acid (HEEDTA), Ethylenediamine di[(2-hydroxy-5-sulfophenyl) acetic acid] (EDDHSA), Ethylenediamine di[(hydroxyphenyl)acetic acid] (EDDHA), Ethylenediamine di[(ortho-hydroxyphenyl)acetic acid] (o,o-EDDHA), Ethylenediamine [(ortho-hydroxyphenyl) acetic acid]-[(para-hydroxyphenyl) acetic acid ([o,p] EDDHA), Ethylenediamine di[(ortho-hydroxy-methylphenyl)acetic acid] (o,o-EDDHMA), Iminodiacetic acid, Iminodisuccinic acid, oxalic acid, tartaric acid, citric acid, nitrilotriacetic acid, glutamic acid; and polyphosphate, tripolyphosphate, sodium trimetaphosphate; diethylenetriamine methyl phosphonic acid, diethylenetriamine pentakis (methylenephosphonic acid), 1,2-diaminoethane tetrakis (methylenephosphonic acid), nitrilotris (methylenephosphonic acid); phosphono butanetricarboxylic acid.

26. The stable herbicide formulation system of any one of claims 1-22, wherein the metal- chelating agent complex is Iron- ethylenediamine di(hydroxyphenyl acetic) acid complex.

27. The stable herbicide formulation system of any one of claims 1-22, wherein the quaternary ammonium moiety in the cationic surfactant is selected from a group comprising bis(hydroxyethyl)methyltallow alkyl ethoxylated chlorides, octadecylmethyl ethoxylated (2EO) quaternary ammonium, octadecylmethyl ethoxylated (15EO) quaternary ammonium, cocoalkylmethyl ethoxylated (2EO) quaternary ammonium, cocoalkylmethyl ethoxylated (15EO) quaternary ammonium, tallowalkylmethyl ethoxylated (5EO) quaternary ammonium, and tallowalkylmethyl ethoxylated (15EO) quaternary ammonium.

28. The stable herbicide formulation system of claim 27, wherein the cationic surfactant is Adsee 611 containing bis(hydroxyethyl)methyltallow alkyl ethoxylated chlorides.

29. The stable herbicide formulation system of any one of claims 1-22, wherein the pH modifier is selected from a group comprising sodium carbonate, sodium bicarbonate, potassium carbonate and potassium bicarbonate.

30. The stable herbicide formulation system of claim 29, wherein the pH modifier is sodium carbonate.

31. The stable herbicide formulation system of any one of claims 1-22, wherein agriculturally acceptable carrier is a wetting agent which is selected from a group comprising Alcohol ethoxylates.

32. The stable herbicide formulation system of claim 31, wherein the wetting agent is Lutensol AT50.

33. The stable herbicide formulation system of any one of claims 1-22, wherein agriculturally acceptable carrier is a filler which is selected from a group comprising China Clay, Precipitated silica and combination thereof.

34. A method of treating a plant against undesired weeds comprising applying herbicide formulation system of any one of claims 1-22, after dilution with water, to the target sites of the field, so as to treat the plant against undesired weeds.

35. The method of claim 34, wherein the undesired weeds are selected from a group comprising grassy and broadleaf weeds.

36. The method of any one of claims 34-35, wherein the undesired weeds are selected from a group comprising Echinochloa spp., Cyperus spp., Ammania spp., Phyllanthus niruri, Digitaria spp., Dactyloctenium spp., Alternenthera sessilis, Commelina communis, Eclipta alba., and Ludvigia spp.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IL2022/051072

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N37/40 A01N39/02 A01N39/04 A01N43/40 A01N43/54
A01P13/02 A01N25/02
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 A01P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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[x] Further documents are listed in the continuation of Box C.
[x] 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
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"P" document published prior to the international filing date but later than the priority date claimed
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"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
16 December 2022	23/12/2022

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Beligny, Samuel

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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