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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 December 2004 (09.12.2004)

PCT

(10) International Publication Number
WO 2004/105482 A2

(51) International Patent Classification[7]: A01N

(21) International Application Number: PCT/EP2004/005254

(22) International Filing Date: 15 May 2004 (15.05.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2003-152242 29 May 2003 (29.05.2003) JP

(71) Applicant *(for all designated States except US)*: **BAYER CROPSCIENCE AG** [DE/DE]; Alfred-Nobel-Str. 50, 40789 Monheim (DE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **ENDO, Keiji** [JP/JP]; 4233-4, Ami, Ami-machi, Inashiki-gun, Ibaraki 300-0331 (JP). **ITO, Seishi** [JP/JP]; 1-41-10, Ekihigashidoori, Oyama-shi, Tochigi 323-0022 (JP). **MUKAIDA, Hideshi** [JP/JP]; 5-25-74, Goshogaoka, Moriya-shi, Ibaraki 302-0119 (JP).

(74) Common Representative: **BAYER CROPSCIENCE AG**; Law and Patents, Patents and Licensing, 51368 Leverkusen (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *without international search report and to be republished upon receipt of that report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: HERBICIDAL COMPOSITIONS FOR PADDY FIELD

(57) Abstract: Herbicidal compositions containing (a) herbicidal benzoylcyclohexadiones and (b) at least one compound selected from the group of compounds represented by the following generic names or code numbers consisting of pyraclonil, HOK201, naproanilide, pyrazolate, pyrazoxifen, clomeprop, cumyluron, dimepiperate, quinoclamine, bensulide, simetryn, butamifos, MCPB and bentazone, as effective components. These compositions have a superior action compared with the herbicides employed individually.

WO 2004/105482 A2

# HERBICIDAL COMPOSITIONS FOR PADDY FIELD

The present invention relates to herbicidal compositions for paddy field. More specifically the present invention relates to herbicidal compositions for paddy field containing herbicidal benzoylcyclohexadiones and certain known herbicidal compounds as effective components.

Herbicidal benzoylcyclohexadiones are known from WO 98/29406; WO 00/21924; WO 01/07422. Several compounds disclosed in these references show good controlling effect against paddy weeds

In practice, however, these compounds do not show satisfactory herbicidal effects and/or phytotoxicity against paddy rice is observed. In practice, however, the use of the benzoylcyclohexanediones known from these publications frequently entails disadvantages. Thus, the herbicidal activity is not always sufficient, or, if the herbicidal activity is sufficient, undesired damage to the rice plants is observed.

The activity of herbicides depends, inter alia, on the type of the herbicide employed, its application rate, the preparation, the harmful plants to be controlled, the climatic conditions and soil conditions and the like. Another criterion is the duration of action or degradation rate of the herbicide. Where appropriate, changes in the sensitivity of harmful plants to an active ingredient, which may occur upon prolonged use or within a geographically defined area, may also have to be taken into account. Such changes manifest themselves as more or less pronounced losses of action and can only be compensated for to a certain extent by increasing the application rates of the herbicides.

Owing to the large number of possible influencing factors, there exists virtually no single active ingredient which combines the desired properties for the various uses, in particular with regard to the species of the harmful plants and the climatic zones. What is more, there are constant demands for achieving the effect with increasingly smaller herbicide rates. A lesser rate reduces not only the amount of an active ingredient required for application, but also, as a rule, the amount of formulation auxiliaries required. Both reduce the financial input and improve the eco-friendliness of the herbicide treatment.

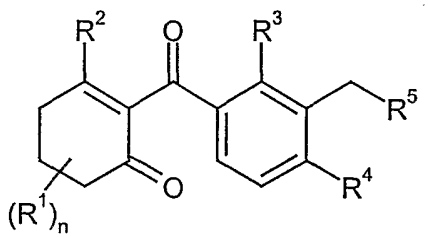
A method which is frequently used for improving the use characteristics of a herbicide is to combine the active ingredient with one or more other active ingredients which contribute the desired additional properties. However, phenomena of physical and biological incompatibility are frequently observed when several active ingredients are

used as a combination, for example lack of stability of a coformulation, degradation of an active ingredient, or antagonism of the active ingredients. In contrast, combinations of active ingredients with an advantageous spectrum of action, high stability and the highest possible synergistically enhanced action, which allows the application rate to be reduced in comparison with the individual application of the active ingredients to be combined, are desired.

It is an object of the present invention to provide herbicidal compositions for use in rice crops, which compositions have improved properties compared with the prior art.

The invention relates to herbicidal compositions comprising an effective content of

(a) at least one of the compounds represented by the formula



(I)

wherein

$R^1$ represents $C_{1-4}$alkyl,

$R^2$ represents O-$R^6$, $SO_m$-$R^7$, cyanato, cyano, thiocyanato or halogen,

$R^3$ and $R^4$ each independently represents hydrogen, halogen, $C_{1-4}$alkyl, halo-$C_{1-4}$alkyl, cyano, nitro or $SO_m$-$R^7$,

$R^5$ represents O-$(CH_2)_p$-O-$(CH_2)_q$-O$R^7$, $C_{3-8}$cycloalkyloxy, $C_{3-8}$cycloalkyl-$C_{1-4}$ alkoxy, 2-tetrahydrofuranylmethoxy, 3-tetrahydrofuranylmethoxy, 2-tetrahydro-2H-pyranylmethoxy, 2-tetrahydrothienylmethoxy, 2-furanylmethoxy or 2-thienylmethoxy,

$R^6$ represents hydrogen, $C_{1-4}$alkyl or halo-$C_{1-4}$alkyl,

$R^7$ represents $C_{1-4}$alkyl, $C_{2-4}$alkenyl, $C_{2-4}$alkynyl, halo-$C_{1-4}$alkyl, halo-$C_{2-4}$alkenyl or halo-$C_{2-4}$alkynyl,

n represents 0, 1, 2, 3, 4, 5 or 6,

m represents 0,1 or 2,

p represents 2, 3 or 4, and

q represents 2, 3 or 4,

or their agriculturally customary salts, ["component a"] and

(b) at least one compound from the group consisting of the compounds represented by the following generic names or code numbers: pyraclonil, HOK201, naproanilide, pyrazolate, pyrazoxifen, clomeprop, cumyluron, dimepiperate, quinoclamine, bensulide, simetryn, butamifos, MCPB and bentazone, ["component b"]

as effective components.

By means of the above-mentioned compositions of the present invention, surprisingly, a substantially higher herbicidal effect, in comparison with the case that each active compound is singly used, than the sum of the individual effect of each of them, is shown. Consequently, it becomes possible, in conducting the weed control, to substantially reduce the concentration of each chemical that has been conventionally used. At the same time, by means of said compositions, a broad herbicidal spectrum can be obtained and the application period can be broadened to a long period of time. For example, in the paddy rice cultivation, they show excellent herbicidal effect in any time of use from the early period of weed-emergence just after transplantation to growing period. Moreover, such an excellent herbicidal effect as durability of effect for a long time, excellent residual effect without phytotoxicity against rice is obtained.

Preferred herbicidal compositions comprise as component a, compound of the formula (I) where:

$R^1$ represents $C_{1-4}$alkyl,

$R^2$ represents O-$R^6$, $SO_m$-$R^7$, cyanato, cyano, thiocyanato or halogen,

$R^3$ and $R^4$ each independently represents hydrogen, halogen, $C_{1-4}$alkyl, halo-$C_{1-4}$alkyl, cyano, nitro or $SO_m$-$R^7$,

$R^5$ represents O-$(CH_2)_p$-O-$(CH_2)_q$-O$R^7$, $C_{3-8}$cycloalkyloxy, $C_{3-8}$cycloalkyl-$C_{1-4}$alkoxy or 2-tetrahydrofuranylmethoxy,

$R^6$ represents hydrogen, $C_{1-4}$alkyl or halo-$C_{1-4}$alkyl,

$R^7$ represents $C_{1-4}$alkyl, $C_{2-4}$alkenyl, $C_{2-4}$alkynyl, halo-$C_{1-4}$alkyl, halo-$C_{2-4}$alkenyl or halo-$C_{2-4}$alkynyl,

n represents 0. 1, 2, 3, 4, 5 or 6,

m represents 0,1 or 2,

p represents 2, 3 or 4, and

q represents 2, 3 or 4,

Particular preferred herbicidal compositions comprise as component (a), a compound of the formula (I) where:

$R^1$ represents methyl,

$R^2$ represents O-$R^6$,

$R^3$ and $R^4$ each independently represents hydrogen, chloro, fluoro, methyl, trifluoromethyl, cyano, nitro or $SO_2$-$R^7$,

$R^5$ represents O-$(CH_2)_p$-O-$(CH_2)_q$-O$R^7$, $C_{3-8}$cycloalkyloxy, $C_{3-8}$cycloalkyl-$C_{1-4}$alkoxy, 2-tetrahydrofuranylmethoxy, 3-tetrahydrofuranylmethoxy, 2-tetrahydro-2H-pyranylmethoxy, 2-tetrahydrothienylmethoxy, 2-furanylmethoxy or 2-thienylmethoxy,

$R^6$ represents hydrogen,

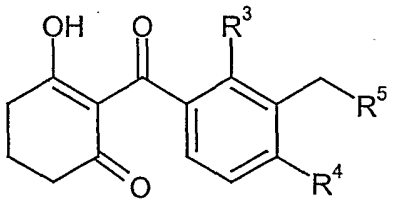
$R^7$ represents methyl or ethyl,

n represents 0. 1 or 2, and

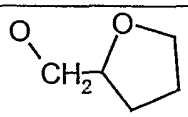
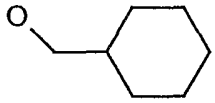
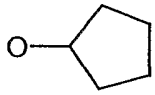
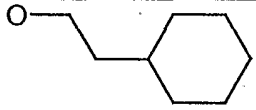
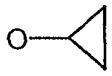
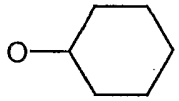
m, p and q each represent 2.

Furthermore preferred are herbicidal compositions that comprise, as component (a), a compound of the formula (Ia) with the meanings stated hereinbelow:

Table 1



(Ia)

| No. | $R^3$ | $R^4$ | $R^5$ |
|---|---|---|---|
| (a-1) | Cl | $SO_2CH_3$ |  |
| (a-2) | Cl | $SO_2CH_3$ |  |
| (a-3) | Cl | $SO_2CH_3$ |  |
| (a-4) | Cl | $SO_2CH_3$ |  |
| (a-5) | Cl | $SO_2CH_3$ | $O(CH_2CH_2O)_2CH_2CH_3$ |
| (a-6) | $CF_3$ | $SO_2CH_2CH_3$ | $O(CH_2CH_2O)_2CH_2CH_3$ |
| (a-7) | Cl | $SO_2CH_2CH_3$ |  |
| (a-8) | Cl | $SO_2CH_2CH_3$ |  |
| (a-9) | $CF_3$ | $SO_2CH_2CH_3$ | $O(CH_2CH_2O)_2CH_3$ |
| (a-10) | $CH_3$ | $SO_2CH_3$ | $O(CH_2CH_2O)_2CH_3$ |
| (a-11) | Cl | $SO_2CH_3$ | $O(CH_2CH_2O)_2CH_3$ |
| (a-12) | $CH_3$ | $SO_2CH_3$ | $O(CH_2CH_2O)_2CH_2CH_3$ |

Preferred as components (b) are (b-1) pyraclonil, (b-2) HOK201, (b-3) naproanilide, (b-4) pyrazolate, (b-5) pyrazoxifen, (b-6) clomeprop, (b-7) cumyluron, (b-8) dimepiperate, (b-9) quinoclamine, (b-10) bensulide, (b-11) simetryn, (b-12) butamifos, (b-13) MCPB and (b-14) bentazone.

Herbicidal compositions which are of particular interest in this context are those with a synergistically active content of one or more of the following combinations of two compounds (A) + (B):

(a-1)+(b-1), (a-1)+(b-2), (a-1)+(b-3), (a-1)+(b-4), (a-1)+(b-5), (a-1)+(b-6), (a-1)+(b-7), (a-1)+(b-8), (a-1)+(b-9), (a-1)+(b-10), (a-1)+(b-11), (a-1)+(b-12), (a-1)+(b-13), (a-1)+(b-14);
(a-2)+(b-1), (a-2)+(b-2), (a-2)+(b-3), (a-2)+(b-4), (a-2)+(b-5), (a-2)+(b-6), (a-2)+(b-7), (a-2)+(b-8), (a-2)+(b-9), (a-2)+(b-10), (a-2)+(b-11), (a-2)+(b-12), (a-2)+(b-13), (a-2)+(b-14);
(a-3)+(b-1), (a-3)+(b-2), (a-3)+(b-3), (a-3)+(b-4), (a-3)+(b-5), (a-3)+(b-6), (a-3)+(b-7), (a-3)+(b-8), (a-3)+(b-9), (a-3)+(b-10), (a-3)+(b-11), (a-3)+(b-12), (a-3)+(b-13), (a-3)+(b-14);
(a-4)+(b-1), (a-4)+(b-2), (a-4)+(b-3), (a-4)+(b-4), (a-4)+(b-5), (a-4)+(b-6), (a-4)+(b-7), (a-4)+(b-8), (a-4)+(b-9), (a-4)+(b-10), (a-4)+(b-11), (a-4)+(b-12), (a-4)+(b-13), (a-4)+(b-14);
(a-5)+(b-1), (a-5)+(b-2), (a-5)+(b-3), (a-5)+(b-4), (a-5)+(b-5), (a-5)+(b-6), (a-5)+(b-7), (a-5)+(b-8), (a-5)+(b-9), (a-5)+(b-10), (a-5)+(b-11), (a-5)+(b-12), (a-5)+(b-13), (a-5)+(b-14);
(a-6)+(b-1), (a-6)+(b-2), (a-6)+(b-3), (a-6)+(b-4), (a-6)+(b-5), (a-6)+(b-6), (a-6)+(b-7), (a-6)+(b-8), (a-6)+(b-9), (a-6)+(b-10), (a-6)+(b-11), (a-6)+(b-12), (a-6)+(b-13), (a-6)+(b-14);
(a-7)+(b-1), (a-7)+(b-2), (a-7)+(b-3), (a-7)+(b-4), (a-7)+(b-5), (a-7)+(b-6), (a-7)+(b-7), (a-7)+(b-8), (a-7)+(b-9), (a-7)+(b-10), (a-7)+(b-11), (a-7)+(b-12), (a-7)+(b-13), (a-7)+(b-14);
(a-8)+(b-1), (a-8)+(b-2), (a-8)+(b-3), (a-8)+(b-4), (a-8)+(b-5), (a-8)+(b-6), (a-8)+(b-7), (a-8)+(b-8), (a-8)+(b-9), (a-8)+(b-10), (a-8)+(b-11), (a-8)+(b-12), (a-8)+(b-13), (a-8)+(b-14);
(a-9)+(b-1), (a-9)+(b-2), (a-9)+(b-3), (a-9)+(b-4), (a-9)+(b-5), (a-9)+(b-6), (a-9)+(b-7), (a-9)+(b-8), (a-9)+(b-9), (a-9)+(b-10), (a-9)+(b-11), (a-9)+(b-12), (a-9)+(b-13), (a-9)+(b-14);
(a-10)+(b-1), (a-10)+(b-2), (a-10)+(b-3), (a-10)+(b-4), (a-10)+(b-5), (a-10)+(b-6), (a-10)+(b-7), (a-10)+(b-8), (a-10)+(b-9), (a-10)+(b-10), (a-10)+(b-11), (a-10)+(b-12), (a-10)+(b-13), (a-10)+(b-14);
(a-11)+(b-1), (a-11)+(b-2), (a-11)+(b-3), (a-11)+(b-4), (a-11)+(b-5), (a-11)+(b-6), (a-11)+(b-7), (a-11)+(b-8), (a-11)+(b-9), (a-11)+(b-10), (a-11)+(b-11), (a-11)+(b-12), (a-11)+(b-13), (a-11)+(b-14);
(a-12)+(b-1), (a-12)+(b-2), (a-12)+(b-3), (a-12)+(b-4), (a-12)+(b-5), (a-12)+(b-6), (a-12)+(b-7), (a-12)+(b-8), (a-12)+(b-9), (a-12)+(b-10), (a-12)+(b-11), (a-12)+(b-12), (a-12)+(b-13), (a-12)+(b-14);

Pyraclonil is described in WO 94/8999 and HOK201 is described in WO 98/38176. Other above-mentioned compounds besides them are mentioned in, for example, The Pesticide Manual 12th edition (published by British Crop Protection Council in 2000).

The herbicidal compounds as components (b) mentioned above can be used each singly or can be used in combination of 2 kinds or more.

In the compositions of the present invention, the mixing ratio of component (a) and component (b) can be varied in a relatively wide range according to the time of application, region of application, method of application, etc. of said compositions. They can be used in the range of generally 1/200 - 200 parts by weight, preferably 1/20 - 20 parts by weight of at least 1 kind of the herbicidal compounds as (b) components for 1 part by weight of a compound of the formula (I) as component (a) or its agriculturally customary salt. More specifically the ratio of use of individual compound of component (b) for 1 part by weight of a compound of the formula (I) as component (a) or its salt can be as follows.

(b-1) pyraclonil: 1/200 – 100 parts by weight, preferably 1/10 - 10 parts by weight,
(b-2) HOK201: 1/200 – 100 parts by weight, preferably 1/10 - 10 parts by weight,
(b-3) naproanilide: 1/100 – 200 parts by weight, preferably 1/10 - 20 parts by weight,
(b-4) pyrazolate: 1/100 – 200 parts by weight, preferably 1/10 - 20 parts by weight,
(b-5) pyrazoxifen :1/200 – 100 parts by weight, preferably 1/10 - 10 parts by weight,
(b-6) clomeprop: 1/200 – 100 parts by weight, preferably 1/10 - 10 parts by weight,
(b-7) cumyluron: 1/100 – 200 parts by weight, preferably 1/10 - 20 parts by weight,
(b-8) dimepiperate: 1/100 – 200 parts by weight, preferably 1/10 - 20 parts by weight,
(b-9) quinoclamine: 1/100 – 200 parts by weight, preferably 1/10 - 20 parts by weight,
(b-10) bensulide: 1/100 – 200 parts by weight, preferably 1/10 - 20 parts by weight,
(b-11) simetryn: 1/200 – 100 parts by weight, preferably 1/10 - 10 parts by weight,
(b-12) butamifos: 1/200 – 100 parts by weight, preferably 1/10 - 10 parts by weight,
(b-13) MCPB: 1/200 – 100 parts by weight, preferably 1/10 - 10 parts by weight,
(b-14) bentazone: 1/100 – 200 parts by weight, preferably 1/10 - 20 parts by weight,

The compositions of the present invention show strong herbicidal effect against paddy weeds. Said compositions can, therefore, be used as herbicidal compositions for paddy field, particularly as selective herbicides for paddy rice

The compositions of the present invention can be used against various weeds that develop in the paddy field. As their examples there can be mentioned the following:

Dicotyledonous plants of the following Genera: *Polygonum, Rorippa, Rotala, Lindernia, Bidens, Dopatrium, Eclipta, Elatine, Gratiola, Lindernia, Ludwigia, Oenanthe, Ranunculus, Deinostema, etc.*

Monocotyledonous plants of the following Genera: *Echinochloa, Panicum, Poa, Cyperus, Monochoria, Fimbristylis, Sagittaria, Eleocharis, Scirpus, Alisma, Aneilema, Blyxa, Eriocaulon, Potamogeton, etc.*

The compositions of the present invention can be used, concretely for example, in relation to the following typical paddy weeds.

Dicotyledonous plants: *Rotala indica Koehne, Lindernia procumbens Philcox, Ludwigia prostrate, Roxburgh, Potamogeton distinctus A. Benn, Elatine triandra Schk, Oenanthe javanica*

Monocotyledonous plants: *Echinochloa oryzicola Vasing, Monochoria vaginalis Presl, Eleocharis, acicularis L., Eleocharis Kuroguwai Ohwi, Cyperus difformis L., Cyperus serotinus, Rottboel, Sagittaria pygmaea Miq, Alisma canaliculatum A. Br. et Bouche, Scirpus juncoides Roxburgh*

The use of the compositions of the present invention, however, should not be restricted to these weeds in any way, but can be applied against other weeds in the same manner.

The compositions of the present invention can be made into customary formulations in case of using for control of the paddy weeds. Formulations are, for example, solutions, emulsions, wettable powders, suspensions, powders, soluble powders, granules, suspo-emulsion concentrates, solid formulations (jumbo formulations), floating granules, microcapsules in polymer substance, etc.

The individual types of formulation are known in principle and are described, for example, in: Winnacker-Küchler, "Chemische Technologie" [Chemical Engineering], Volume 7, C. Hauser Verlag Munich, 4th Ed. 1986; van Valkenburg, "Pesticides Formulations", Marcel Dekker N.Y., 1973; K. Martens, "Spray Drying Handbook", 3rd Ed. 1979, G. Goodwin Ltd. London. The formulation auxiliaries required, such as inert materials, surfactants, solvents and further additives, are likewise known and are described, for example, in: Watkins, "Handbook of Insecticide Dust Diluents and Carriers", 2nd Ed., Darland Books, Caldwell N.J.; H.v. Olphen, "Introduction to Clay Colloid Chemistry"; 2nd Ed., J. Wiley & Sons, N.Y. Marsden, "Solvents Guide", 2nd Ed., Interscience, N.Y. 1950; McCutcheon's, "Detergents and Emulsifiers Annual", MC Publ. Corp., Ridegewood N.J.; Sisley and Wood,

"Encyclopedia of Surface Active Agents", Chem. Publ. Co. Inc., N.Y. 1964; Schönfeldt, "Grenzflächenaktive Äthylenoxidaddukte" [Surface-active ethylene oxide adducts], Wiss. Verlagsgesellschaft, Stuttgart 1976, Winnacker-Küchler, "Chemische Technologie", Volume 7, C. Hauser Verlag Munich, 4th Ed. 1986.

Based on these formulations, combinations with other pesticidally active substances, such as other herbicides, fungicides or insecticides, and with safeners, fertilizers and/or growth regulators, may also be prepared, for example in the form of a readymix or a tank mix.

These formulations can be prepared according to per se known methods. The formulations according to the present invention can be prepared, for example, by mixing the aforementioned component (a) and component (b) with extenders, namely liquid diluents and/or solid diluents, and optionally with surfactants, namely emulsifiers and/or dispersants and/or foam-forming agents.

In case of using water as extender, organic solvents can be used as auxiliary solvent. As liquid diluents there can be mentioned, for example, organic solvents such as aromatic hydrocarbons (for example, xylene, toluene, alkylnaphthalene, etc.), chlorinated aromatic or chlorinated aliphatic hydrocarbons (for example, chlorobenzenes, ethylene chlorides, methylene chloride, etc.), aliphatic hydrocarbons [for example, cyclohexane etc. or paraffins (for example, mineral oil fractions, mineral and vegetable oils, etc.)], alcohols (for example, butanol, glycol and their ethers, esters, etc.), ketones (for example, acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, etc.), strongly polar solvents (for example, dimethylformamide, dimethyl sulfoxide, etc.), and water.

Solid diluents are, for example, ammonium salts and ground natural minerals (for example, kaolin, clay, talc, chalk, quartz, attapulgite, montmorillonite, diatomaceous earth, etc.), ground synthetic minerals (for example, highly dispersed silicic acid, alumina, silicates, etc.) etc. As solid carriers for granules there can be used, for example, crushed and fractionated rocks (for example, calcite, marble, pumice, sepiolite, dolomite, etc.) synthetic granules of inorganic and organic meals, particles of organic materials (for example, saw dust, coconut shells, maize cobs, tobacco stalks, etc.) etc.

Emulsifiers and/or foam-forming agents are, for example, nonionic and anionic emulsifiers [for example, polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers (for example, alkylaryl polyglycol ethers, alkylsulfonates, alkylsulfates, arylsulfonates, etc.)], albumin hydrolysis products, etc.

Dispersants are, for example, lignin sulfite waste liquor and methyl cellulose are adequate.

Tackifiers can also be used in formulations (powders, granules, emulsifiable concentrates). Tackifiers are, for example, carboxymethyl cellulose, natural and synthetic polymers (for example, gum Arabic, polyvinyl alcohol, polyvinyl acetates, etc.) natural phospholipids (for example, cephalins and recithins), synthetic phospholipids, etc.

As additives, mineral oils and vegetable oils can be used.

Colorants can also be used. Colorants are, for example, inorganic pigments (for example, iron oxide, titanium oxide, Prussian Blue, etc,), organic dyestuffs such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs, and further traces nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations can contain the total of component (a) and component (b) in the range of concentration of generally 0.1-95 % by weight, preferably 0.5-90 % by weight.

The compositions of the present invention can be used for weed control as themselves or in their formulation forms. It is possible to do tank mixing when they are used, and further to mix with other known active compounds, particularly active compounds generally used for paddy field, for example, fungicides, insecticides, plant growth regulators, plant nutrients, soil improving agents, safeners and other herbicides. As a favorable example, for example, 1-($\alpha$,$\alpha$-dimethylbenzyl)-3-p-tolylurea as a safener can be added at an amount in the range of 1-200 parts by weight, preferably 2-100 parts by weight for 1 part by weight of a compound (a) of the formula (I) in the compositions of the present invention.

The compositions of the present invention can be directly used as such or in their formulation forms or in application forms prepared by further diluting said formulations, for example, in the forms of ready-to-use solutions, emulsifiable concentrates, suspensions, powders, wettable powders or granules. Formulations of these forms can be applied to paddy field by usual methods, for example, watering, spraying, atomizing, dusting, granule application, etc.

The compositions of the present invention can be applied to paddy field before, during or after transplantation. The applicable amount of said compositions can be varied in a substantial range. The application amount can be, as the total amount of the component

(a) and component (b), for example, in the range of 0.01-5 kg/ha, preferably 0.06-4.5 kg/ha.

Excellent results of the compositions by the present invention will be described more specifically by the following examples. The present invention, however, should not be restricted only to them in any way.

**EXAMPLES**

Biological test examples and formulation examples

Preparation of test solution

Carrier: Acetone 5 parts by weight

Surfactant: Benzyloxy polyglycol ether 1 part by weight

A prescribed amount of the test solution is prepared by diluting with water the formulation obtained by mixing the above-mentioned carrier and surfactant with 1 part by weight of the active compounds (component (a) or component (b)).

Test Example 1: Test of effect of herbicidal compositions against paddy weeds

Two sets of 3 seedlings of paddy rice (variety: Nihonbare) of 2.5 leaf stage (15cm tall) were transplanted in a 1/2,000a pot (25x20x9cm) filled with paddy soil.

Then seeds of *Echinochloa oryzicola Vasing, Cyperus serotinus Rottboel, Monochoria vaginalis Presl, Scirpus juncoides Roxburgh* and tubers of *Sagittaria pygmaea Miq* were inoculated and water was poured to a depth of about 2-3 cm. Five days after the rice transplantation a test solution prepared by the aforementioned method or its mixture was applied to the surface of water. After the treatment the water depth of 3cm was maintained and the herbicidal effect was evaluated after 4 weeks from the treatment by the following standard (shown in %).

100%: Complete withering

0%: No effect or no phytotoxicity

Test results are shown in Table 1.

**Table 1**

| Compound | Amount of effective component g/ha | Herbicidal effect | | | | |
|---|---|---|---|---|---|---|
| | | *Echinochloa oryzicola Vasing* | *Monochoria vaginalis Presl* | *Scirpus juncoides Roxburgh* | *Sagittaria pygmaea Miq* | *Cyperus serotinus Rottboel* |
| (a–1) | 18+50 | 90 | 100 | 60 | 80 | — |
| + (b–1) | 18+100 | 100 | 100 | 80 | 80 | — |
| | 37.5+25 | 80 | 100 | 80 | 90 | 50 |
| | 37.5+50 | 100 | 100 | 80 | 100 | 50 |
| | 37.5+100 | 100 | 100 | 90 | 100 | 80 |
| | 75+25 | 100 | 100 | 90 | 100 | 50 |
| | 75+50 | 100 | 100 | 90 | 100 | 60 |
| | 75+100 | 100 | 100 | 100 | 100 | 90 |
| (a–1) | 18+18.7 | 80 | 100 | — | 70 | — |
| + (b–2) | 18+37.5 | 80 | 100 | — | 90 | — |
| | 18+75 | 95 | 100 | 50 | 90 | — |
| | 37.5+18.7 | 80 | 100 | 50 | 80 | — |
| | 37.5+37.5 | 90 | 100 | 70 | 100 | — |
| | 37.5+75 | 100 | 100 | 70 | 100 | 50 |
| (a–1) | 18+500 | — | 100 | — | — | — |
| + (b–3) | 18+1000 | — | 100 | 50 | — | — |
| | 37.5+500 | — | 100 | 60 | 90 | — |
| | 37.5+1000 | — | 100 | 70 | 90 | 50 |
| | 75+2000 | 80 | 100 | 90 | 100 | 60 |
| (a–1) | 37.5+250 | — | 100 | — | 100 | — |
| + (b–4) | 37.5+500 | — | 100 | 60 | 100 | — |
| | 75+250 | — | 100 | 80 | 100 | 80 |
| | 75+500 | 80 | 100 | 80 | 100 | 80 |

**Table 1 (continued)**

| Compound | Amount of effective component g/ha | Herbicidal effect | | | | |
|---|---|---|---|---|---|---|
| | | *Echinochloa oryzicola Vasing* | *Monochoria vaginalis Presl* | *Scirpus juncoides Roxburgh* | *Sagittaria pygmaea Miq* | *Cyperus serotinus Rottboel* |
| (a–1) | 37.5+250 | — | 100 | — | 90 | — |
| + (b–5) | 37.5+500 | — | 100 | — | 100 | — |
| | 75+1000 | 80 | 100 | 80 | 100 | 80 |
| | 75+2000 | 90 | 100 | 90 | 100 | 80 |
| (a–1) | 37.5+37.5 | — | 100 | 60 | 90 | — |
| +(b–6) | 37.5+75 | — | 100 | 70 | 90 | 50 |
| | 75+150 | 80 | 100 | 90 | 100 | 60 |
| | 75+300 | 80 | 100 | 90 | 100 | 70 |
| (a–1) | 37.5+93 | — | 100 | — | — | — |
| + (b–7) | 75+93 | — | 100 | 70 | 80 | 80 |
| | 150+93 | 100 | 100 | 90 | 100 | 80 |
| (a–1) | 37.5+750 | 80 | 100 | 80 | 80 | 50 |
| + (b–8) | 37.5+1500 | 90 | 100 | 80 | 80 | 70 |
| (a–1) | 18+113 | — | 100 | — | — | |
| + (b–9) | 75+450 | 70 | 100 | 70 | 100 | 90 |
| (a–1) | 37.5+93.5 | 70 | 100 | 60 | 80 | — |
| + (b–10) | 37.5+187 | 80 | 100 | 80 | 90 | — |
| | 37.5+375 | 80 | 100 | 80 | 90 | 90 |
| (a–1) | 37.5+100 | 100 | 100 | 80 | 100 | — |
| + (b–11) | 75+100 | 100 | 100 | 90 | 100 | 80 |

| Compound | Amount of effective component g/ha | Herbicidal effect | | | | |
|---|---|---|---|---|---|---|
| | | *Echinochloa oryzicola Vasing* | *Monochoria vaginalis Presl* | *Scirpus juncoides Roxburgh* | *Sagittaria pygmaea Miq* | *Cyperus serotinus Rottboel* |
| (a–1) + (b–12) | 18+125 | — | 100 | — | — | — |
| | 75+250 | 60 | 100 | 80 | 80 | — |
| | 75+500 | 70 | 100 | 80 | 80 | — |
| | 75+1000 | 90 | 100 | 85 | 90 | — |
| | 300+500 | 100 | 100 | 100 | 98 | 100 |
| (a–1) + (b–13) | 37.5+15 | — | 100 | — | 80 | — |
| | 75+120 | 80 | 100 | 90 | 100 | 80 |
| (a–1) + (b–14) | 18+187 | — | 100 | — | 60 | — |
| | 75+187 | 80 | 100 | 60 | 100 | 60 |
| | 75+375 | 90 | 100 | 80 | 100 | 80 |
| (a–1) | 18 | 50 | 60 | 20 | 50 | 0 |
| | 37.5 | 50 | 80 | 30 | 70 | 20 |
| | 75 | 60 | 100 | 50 | 90 | 40 |
| | 150 | 90 | 100 | 80 | 100 | 60 |
| | 300 | 100 | 100 | 95 | 100 | 90 |
| (b-1) | 25 | 30 | 100 | 0 | 0 | 0 |
| | 50 | 50 | 100 | 20 | 0 | 0 |
| | 100 | 80 | 100 | 30 | 0 | 0 |
| (b-2) | 18.7 | 50 | 70 | 0 | 0 | 0 |
| | 37.5 | 50 | 90 | 0 | 0 | 0 |
| | 75 | 80 | 90 | 0 | 20 | 0 |
| (b-3) | 500 | 0 | 70 | 0 | 0 | 0 |

| Compound | Amount of effective component g/ha | Herbicidal effect | | | | |
|---|---|---|---|---|---|---|
| | | *Echinochloa oryzicola Vasing* | *Monochoria vaginalis Presl* | *Scirpus juncoides Roxburgh* | *Sagittaria pygmaea Miq* | *Cyperus serotinus Rottboel* |
| | 1000 | 0 | 80 | 0 | 40 | 0 |
| | 2000 | 0 | 100 | 30 | 60 | 0 |
| (b-4) | 250 | 0 | 80 | 0 | 0 | 0 |
| | 500 | 0 | 90 | 0 | 80 | 0 |
| (b-5) | 250 | 0 | 0 | 0 | 0 | 0 |
| | 500 | 0 | 80 | 0 | 0 | 0 |
| | 1000 | 0 | 90 | 0 | 80 | 0 |
| | 2000 | 0 | 100 | 0 | 100 | 0 |
| (b-6) | 37.5 | 0 | 70 | 0 | 0 | 0 |
| | 75 | 0 | 80 | 0 | 0 | 0 |
| | 150 | 0 | 100 | 30 | 0 | 0 |
| | 300 | 0 | 100 | 70 | 0 | 0 |
| (b-7) | 93 | 0 | 0 | 0 | 0 | 0 |
| (b-8) | 750 | 50 | 0 | 0 | 0 | 0 |
| | 1500 | 70 | 20 | 0 | 0 | 30 |
| (b-9) | 113 | 0 | 0 | 0 | 0 | 0 |
| | 450 | 0 | 30 | 0 | 0 | 0 |
| (b-10) | 93.5 | 30 | 0 | 0 | 0 | 0 |
| | 187 | 40 | 0 | 20 | 0 | 0 |
| | 375 | 50 | 30 | 40 | 0 | 0 |
| (b-11) | 100 | 50 | 0 | 0 | 0 | 0 |

| Compound | Amount of effective component g/ha | Herbicidal effect | | | | |
|---|---|---|---|---|---|---|
| | | *Echinochloa oryzicola Vasing* | *Monochoria vaginalis Presl* | *Scirpus juncoides Roxburgh* | *Sagittaria pygmaea Miq* | *Cyperus serotinus Rottboel* |
| (b-12) | 125 | 20 | 90 | 10 | 0 | 0 |
| | 250 | 40 | 100 | 30 | 0 | 5 |
| | 500 | 60 | 100 | 30 | 0 | 5 |
| | 1000 | 70 | 100 | 40 | 0 | 5 |
| (b-13) | 15 | 0 | 0 | 0 | 0 | 0 |
| | 120 | 0 | 80 | 0 | 0 | 0 |
| (b-14) | 187 | 0 | 0 | 0 | 0 | 0 |
| | 375 | 0 | 0 | 0 | 0 | 0 |

Formulation Example 1: To a mixture of 3 parts by weight of the active compound (a-1), 4 parts by weight of the active compound (b-1), 32 parts by weight of bentonite (montmorillonite), 58 parts by weight of talc and 3 parts by weight of ligninsulfonate salt, 25 parts by weight of water were added, well kneaded, made into granules of 10-40 mesh by an extrusion granulator and dried at 40-50°C to obtain granules.

Formulation Example 2: 96 Parts by weight of clay mineral particles having particle diameter distribution in the range of 0.2-2mm are put in a rotary mixer. While rotating it, 2 parts by weight of the active compound (a-1) and 2 parts by weight of the active compound (b-2) are sprayed together with a liquid diluent, wetted the particles uniformly and dried at 40-50°C to obtain granules.

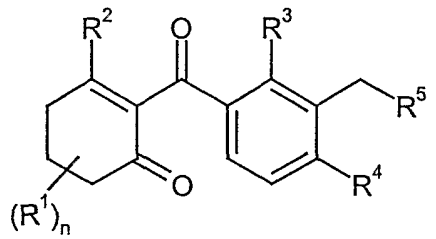
Formulation Example 3: A mixture of 4 parts by weight of the active compound (a-1), 4 parts by weight of the active compound (b-12), 10 parts by weight of ethylene glycol, 3 parts by weight of polyoxyalkylene tristyrylphenyl ether, 10 parts by weight of xanthan gum, 0.5 parts by weight of 14% silicone oil emulsion and 68.5 parts by weight of water was well stirred and then crushed with a crusher (Dyno-Mill Type KDL) to obtain water suspension formulation.

Formulation Example 4: 5 Parts by weight of the active compound (a-1), 15 parts by weight of the active compound (b-11), 30 parts by weight of sodium ligninsulfonate, 15 parts by weight of bentonite and 35 parts by weight of calcined diatomaceous earth powder were sufficiently mixed and, after addition of water, well kneaded, extruded with 0.3 mm screen and dried to obtain water-dispersible granules.

## Claims

1. Herbicidal compositions comprising

(a) at least one of the compounds represented by the formula



(I)

wherein

$R^1$ represents $C_{1-4}$alkyl,

$R^2$ represents O-$R^6$, $SO_m$-$R^7$, cyanato, cyano, thiocyanato or halogen,

$R^3$ and $R^4$ each independently represents hydrogen, halogen, $C_{1-4}$alkyl, halo-$C_{1-4}$alkyl, cyano, nitro or $SO_m$-$R^7$,

$R^5$ represents O-$(CH_2)_p$-O-$(CH_2)_q$-$OR^7$, $C_{3-8}$cycloalkyloxy, $C_{3-8}$cycloalkyl-$C_{1-4}$alkoxy, 2-tetrahydrofuranylmethoxy, 3-tetrahydrofuranylmethoxy, 2-tetrahydro-2H-pyranylmethoxy, 2-tetrahydrothienylmethoxy, 2-furanylmethoxy or 2-thienylmethoxy,

$R^6$ represents hydrogen, $C_{1-4}$alkyl or halo-$C_{1-4}$alkyl,

$R^7$ represents $C_{1-4}$alkyl, $C_{2-4}$alkenyl, $C_{2-4}$alkynyl, halo-$C_{1-4}$alkyl, halo-$C_{2-4}$alkenyl or halo-$C_{2-4}$alkynyl,

n represents 0. 1, 2, 3, 4, 5 or 6,

m represents 0,1 or 2,

p represents 2, 3 or 4, and

q represents 2, 3 or 4,

or their agriculturally customary salts, and

(b) at least one compound selected from the group consisting of pyraclonil, HOK201, naproanilide, pyrazolate, pyrazoxifen, clomeprop, cumyluron, dimepiperate, quinoclamine, bensulide, simetryn, butamifos, MCPB and bentazone.

2. Compositions according to Claim 1

wherein

$R^1$ represents methyl,

$R^2$ represents O-$R^6$,

$R^3$ and $R^4$ each independently represents hydrogen, chloro, fluoro, methyl, trifluoromethyl, cyano, nitro or $SO_2$-$R^7$,

$R^5$ represents O-$(CH_2)_p$-O-$(CH_2)_q$-O$R^7$, $C_{3-8}$cycloalkyloxy, $C_{3-8}$cycloalkyl-$C_{1-4}$alkoxy, 2-tetrahydrofuranylmethoxy, 3-tetrahydrofuranylmethoxy, 2-tetrahydro-2H-pyranylmethoxy, 2-tetrahydrothienylmethoxy, 2-furanylmethoxy or 2-thienylmethoxy,

$R^6$ represents hydrogen,

$R^7$ represents methyl or ethyl,

n represents 0. 1 or 2, and

m, p and q each represents 2,

in the compounds of the formula (I).

3. Compositions according to Claim 1

wherein

$R^1$ represents $C_{1-4}$alkyl,

$R^2$ represents O-$R^6$, $SO_m$-$R^7$, cyanato, cyano, thiocyanato or halogen,

$R^3$ and $R^4$ each independently represents hydrogen, halogen, $C_{1-4}$alkyl, halo-$C_{1-4}$alkyl, cyano, nitro or $SO_m$-$R^7$,

$R^5$ represents $O-(CH_2)_p-O-(CH_2)_q-OR^7$, $C_{3-8}$cycloalkyloxy, $C_{3-8}$cycloalkyl-$C_{1-4}$alkoxy or 2-tetrahydrofuranylmethoxy,

$R^6$ represents hydrogen, $C_{1-4}$alkyl or halo-$C_{1-4}$alkyl,

$R^7$ represents $C_{1-4}$alkyl, $C_{2-4}$alkenyl, $C_{2-4}$alkynyl, halo-$C_{1-4}$alkyl, halo-$C_{2-4}$alkenyl or halo-$C_{2-4}$alkynyl,

n represents 0. 1, 2, 3, 4, 5 or 6,

m represents 0,1 or 2,

p represents 2, 3 or 4, and

q represents 2, 3 or 4,

in the compounds of the formula (I).

4. Compositions according to any of claims 1 - 3 wherein the ratio by weight of component a : component b is between 200:1 and 1:200.

5. Compositions according to any of claims 1 - 3 wherein the ratio by weight of component a : component b is between 20:1 and 1:20.

6. Use of compositions according to any of claims 1 - 3 for controlling undesired vegetation.

7. Use of compositions according to any of claims 1 - 3 for controlling weeds in paddy.

8. Process for preparing herbicidal compositions, characterized in that active compound combinations according to any of Claims 1 to 5 are mixed with extenders and/or surfactants.