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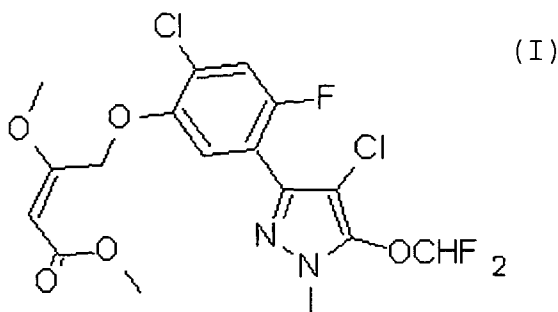
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(54) Title: NEW SYNERGISTIC HERBICIDAL COMPOSITIONS



(57) Abstract: Synergistic compositions are described, having a high herbicidal activity and containing the compound having formula (I) : in a mixture with one or more known herbicidal products.

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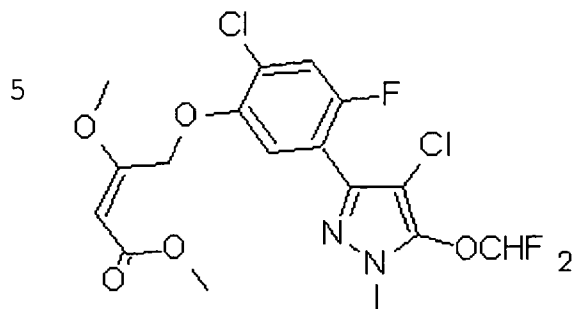
NEW SYNERGISTIC HERBICIDAL COMPOSITIONS

The present invention relates to new herbicidal compositions.

10 More specifically, the present invention relates to new compositions comprising a particular derivative of 3-methoxy-2-butenic acid in a synergistic mixture with one or more known herbicides, and the use thereof as herbicides for the control of weeds in agricultural crops.

15 European patent applications EP 796845 and EP 1020448 describe 3-arylheterocyclic products with a herbicidal activity and the use thereof for the control of weeds in agricultural crops. These documents generically envisage the association of the compounds claimed with
20 other herbicidal products, but no information is provided either as to what the herbicidal compounds suitable for the purpose are, or what are the possible enhancing effects of these compositions compared with the use of 3-arylheterocyclic compounds alone on the herbicidal activity
25 with respect to weeds.

The Applicant has now surprisingly found that when the derivative of 3-methoxy-2-butenic acid having general formula (I),



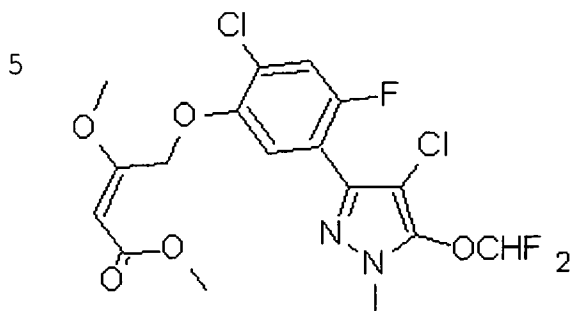
(I)

10 i.e. methyl (E)-4-[2-chloro-5-(4-chloro-5-difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxy]-3-methoxybut-2-enoate, corresponding to Compound N. 2 of EP1020448, is used in association with at least one of the herbicidal products selected from those specified
15 hereunder, it produces synergistic herbicidal mixtures, i.e. mixtures having a much more enhanced herbicidal activity with respect to weeds compared with what is expected based on the activities of products used separately.

20 The phytotoxicity with respect to agricultural crops, on the contrary, remains unvaried, or even lower than the expected value, thus allowing considerable advantages to be obtained in the practical use of these mixtures.

25 An object of the present invention therefore relates

to synergistic herbicidal compositions comprising a component [A] and a component [B], wherein the component [A] is the compound having formula (I)



10

(I)

methyl (E)-4-[2-chloro-5-(4-chloro-5-difluoro-methoxy-1-methylpyrazol-3-yl)-4-fluorophenoxy]-3-methoxy-but-2-enoate, and component [B] consists of at least one product selected from the following herbicides

15

[1] acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide);

[2] alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide);

20

[3] amidosulfuron (N-[[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]-N-methylmethanesulfonamide);

[4] atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine);

25

[5] beflubutamid (2-[4-fluoro-3-(trifluoromethyl)-phenoxy]-N-(phenylmethyl)butanamide);

- [6] bensulfuron-methyl (methyl [[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]-benzoate);
- [7] bispyribac-sodium (sodium 2,6-bis[(4,6-dimethoxy-2-pyrimidinyl)oxy]benzoate);
- [8] bromoxynil (3,5-dibromo-4-hydroxybenzonitrile);
- [9] chlorimuron-ethyl (ethyl [[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate;
- [10] chlorotoluron (N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea);
- [11] chlorsulfuron (2-chloro-N-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide);
- [12] clodinafop-propargyl (propynyl (R)-2-[4-[(5-chloro-3-fluoro-2-pyridinyl)oxy]phenoxy]propanoate);
- [13] clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone);
- [14] diflufenican (N-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridinecarboxamide);
- [15] dimethenamid ((RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide);
- [16] diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea);
- [17] ethoxysulfuron (1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethoxyphenoxy)urea);
- [18] fenoxaprop-P ((R)-2-[4-[(6-chloro-2-benzoxazolyl)-oxy]phenoxy]propanoic acid) and its ethyl ester;

- [19] flufenacet (N-(4-fluorophenyl)-N-(1-methylethyl)-2-
[[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy]-
acetamide);
- [20] fluometuron (N,N-dimethyl-N'-[3-(trifluoromethyl)-
5 phenyl]urea);
- [21] fluroxypyr ([4(4-amino-3,5-dichloro-6-fluoro-2-
pyridinyl)oxy]acetic acid);
- [22] glufosinate (ammonium ($\pm$)-2-amino-4-(hydroxymethyl-
phosphinyl)butanoate);
- 10 [23] glyphosate (N-(phosphonomethyl)glycine) and its
salts;
- [24] halosulfuron (3-chloro-5-[[[(4,6-dimethoxy-2-
pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-
pyrazole-4-carboxylic acid) and its methyl ester;
- 15 [25] imazamox (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-
5-oxo-1H-imidazol-2-yl]-5-(methoxymethyl)-3-
pyridinecarboxylic acid);
- [26] ioxynil (4-hydroxy-3,5-diiodobenzonitrile);
- [27] isoproturon (N,N-dimethyl-N'-[4-(1-methylethyl)-
20 phenyl]urea);
- [28] isoxaflutole ((5-cyclopropyl-4-isoxazolyl)-[2-
(methylsulfonyl)-4-(trifluoromethyl)phenyl]methanone);
- [29] linuron (N'-(3,4-dichlorophenyl)-N-methoxy-N-methyl-
urea);
- 25 [30] MCPA ((4-chloro-2-methylphenoxy)acetic acid) and its

thioethyl ester;

[31] MCPB (4-(4-chloro-2-methylphenoxy)butanoic acid);

[32] mesotrione (2-[4-(methylsulfonyl)-2-nitrobenzoyl]-1,3-cyclohexandione);

5 [33] metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide);

[34] S-metolachlor (mixture of two enantiomers of metolachlor, containing 80-100% of 2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]-

10 acetamide);

[35] metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one);

[36] metsulfuron-methyl (methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]-

15 sulfonyl]-benzoate);

[37] MSMA (monosodium methyl arsonate);

[38] orthosulfamuron (2-[[[[(4,6-dimethoxy-2-pyrimidin-yl)amino]carbonyl]amino]sulfonyl]amino-N,N-dimethylbenzamide);

20 [39] pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine);

[40] penoxsulam (2-(2,2-difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide);

25 [41] pethoxamid (2-chloro-N-(2-ethoxyethyl)-N-(2-methyl-

1-phenyl-1-propenyl)acetamide);

[42] picolinafen (N-(4-fluorophenyl)-6-[3-(trifluoromethyl)phenoxy]-2-pyridinecarboxamide);

[43] pinoxaden (8-(2,6-diethyl-4-methylphenyl)-1,2,4,5-tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropanoate);

[44] prometryn (N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine;

[45] propachlor (2-chloro-N-(methylethyl)-N-phenylacetamide);

[46] propanil (N-(3,4-dichlorophenyl)propanamide);

[47] propoxycarbazone (methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1H-1,2,4-triazol-1-yl)carbonyl]amino]-sulfonyl]benzoate);

[48] sulcotrione (2-[2-chloro-4-(methylsulfonyl)-benzoyl]-1,3-cyclohexanedione);

[49] sulfosulfuron (N-[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]-2-(ethylsulfonyl)imidazo[1,2-a]pyridin-3-sulfonamide);

[50] terbuthylazine (6-chloro-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine);

[51] thifensulfuron-methyl (methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate);

[52] triasulfuron (2-(2-chloroethoxy)-N-[(4-methoxy-6-

methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide);

[53] tribenuron-methyl (methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]-

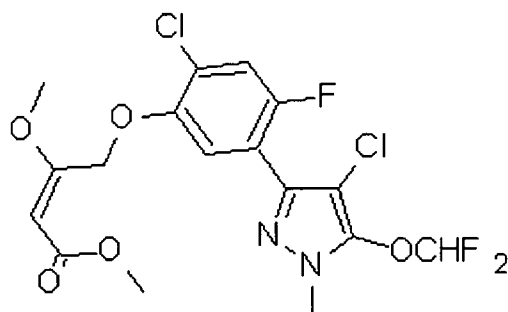
5 sulfonyl]benzoate);

[54] trifloxysulfuron (N-[[[(4,6-dimethoxy-2-pyrimidin-2-yl)amino]carbonyl]-3-(2,2,2-trifluoroethoxy)-2-pyridine-sulfonamide);

[55] trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoro-
10 methyl)benzeneamine).

An object of the present invention also relates to the use of synergistic herbicidal compositions comprising a component [A] and a component [B], wherein component [A] is the compound having formula (I)

15



20

(I)

methyl (E)-4-[2-chloro-5-(4-chloro-5-difluoro-methoxy-1-methylpyrazol-3-yl)-4-fluorophenoxy]-3-methoxy-but-2-enoate, and component [B] consists of at least one product selected from the following herbicides:

25

- [1] acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide);
- [2] alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide);
- 5 [3] amidosulfuron (N-[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]-N-methylmethanesulfonamide);
- [4] atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine);
- 10 [5] beflubutamid (2-[4-fluoro-3-(trifluoromethyl)-phenoxy]-N-(phenylmethyl)butanamide);
- [6] bensulfuron-methyl (methyl [[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]-benzoate);
- 15 [7] bispyribac-sodium (sodium 2,6-bis[(4,6-dimethoxy-2-pyrimidinyl)oxy]benzoate);
- [8] bromoxynil (3,5-dibromo-4-hydroxybenzonitrile);
- [9] chlorimuron-ethyl (ethyl [[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate);
- 20 [10] chlorotoluron (N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea);
- [11] chlorsulfuron (2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide);
- [12] clodinafop-propargyl (propynyl (R)-2-[4-[(5-chloro-3-fluoro-2-pyridinyl)oxy]phenoxy]propanoate);
- 25

- [13] clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone;
- [14] diflufenican (N-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridinecarboxamide);
- 5 [15] dimethenamid ((RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide);
- [16] diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea);
- [17] ethoxysulfuron (1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethoxyphenoxy)sulfonyl)urea);
- 10 [18] fenoxaprop-P ((R)-2-[4-[(6-chloro-2-benzoxazolyl)-oxy]phenoxy]propanoic acid) and its ethyl ester;
- [19] flufenacet (N-(4-fluorophenyl)-N-(1-methylethyl)-2-[[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy]-acetamide);
- 15 [20] fluometuron (N,N-dimethyl-N'-[3-(trifluoromethyl)-phenyl]urea;
- [21] fluroxypyr ([4(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid);
- [22] glufosinate (ammonium ($\pm$)-2-amino-4-(hydroxymethyl-20 phosphinyl)butanoate);
- [23] glyphosate (N-(phosphonomethyl)glycine) and its salts;
- [24] halosulfuron (3-chloro-5-[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-25 pyrazole-4-carboxylic acid) and its methyl ester;

- [25] imazamox (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-(methoxymethyl)-3-pyridinecarboxylic acid;
- [26] ioxynil (4-hydroxy-3,5-diiodobenzonitrile);
- 5 [27] isoproturon (N,N-dimethyl-N'-[4-(1-methylethyl)-phenyl]urea);
- [28] isoxaflutole ((5-cyclopropyl-4-isoxazolyl)-[2-(methylsulfonyl)-4-(trifluoromethyl)phenyl]methanone);
- [29] linuron (N'-(3,4-dichlorophenyl)-N-methoxy-N-methyl-10 urea);
- [30] MCPA ((4-chloro-2-methylphenoxy)acetic acid) and its thioethyl ester;
- [31] MCPB (4-(4-chloro-2-methylphenoxy)butanoic acid);
- [32] mesotrione (2-[4-(methylsulfonyl)-2-nitrobenzoyl]-15 1,3-cyclohexandione);
- [33] metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide);
- [34] S-metolachlor (mixture of two enantiomers of metolachlor, containing 80-100% of 2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]-20 acetamide);
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- [36] metsulfuron-methyl (methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]-25

- sulfonyl]-benzoate);
- [37] MSMA (monosodium methyl arsonate);
- [38] orthosulfamuron (2-[[[[(4,6-dimethoxy-2-pyrimidin-yl)amino]carbonyl]amino]sulfonyl]amino-N,N-dimethyl-
5 benzamide);
- [39] pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine);
- [40] penoxsulam (2-(2,2-difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)
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- [41] pethoxamid (2-chloro-N-(2-ethoxyethyl)-N-(2-methyl-1-phenyl-1-propenyl)acetamide);
- [42] picolinafen (N-(4-fluorophenyl)-6-[3-(trifluoromethyl)phenoxy]-2-pyridinecarboxamide);
- 15 [43] pinoxaden (8-(2,6-diethyl-4-methylphenyl)-1,2,4,5-tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropanoate);
- [44] prometryn (N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine;
- 20 [45] propachlor (2-chloro-N-(methylethyl)-N-phenylacetamide);
- [46] propanil (N-(3,4-dichlorophenyl)propanamide);
- [47] propoxycarbazone (methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1H-1,2,4-triazol-1-yl)carbonyl]amino]-
25 sulfonyl]benzoate);

- [48] sulcotrione (2-[2-chloro-4-(methylsulfonyl)-benzoyl]-1,3-cyclohexanedione);
- [49] sulfosulfuron (N-[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]-2-(ethylsulfonyl)imidazo[1,2-a]pyridin-3-sulfonamide);
- [50] terbuthylazine (6-chloro-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine);
- [51] thifensulfuron-methyl (methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate);
- [52] triasulfuron (2-(2-chloroethoxy)-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide);
- [53] tribenuron-methyl (methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]sulfonyl]benzoate);
- [54] trifloxysulfuron (N-[[(4,6-dimethoxy-2-pyrimidin-2-yl)amino]carbonyl]-3-(2,2,2-trifluoroethoxy)-2-pyridine-sulfonamide);
- [55] trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzeneamine);

for the control of weeds in agricultural crops.

In particular, component [B] is preferably selected from bromoxynil, diflufenican, flufenacet, glyphosate, ioxynil, isoproturon, mesotrione, S-metolachlor.

Component [A], a compound having formula (I), can be prepared according to the method described in EP1020448 and as specified in detail in Example 1 described below.

The components [B] are known commercial products or
5 products in the commercialization phase and are therefore indicated with their common ISO (International Standard Organization) name and with the chemical names according to Chemical Abstracts. The structural formulae of these products, as also the main applications as herbicides are
10 specified, among others, in "The Pesticide Manual" 13^a edition (2003), Ed. C.D.S. Tomlin, published by the British Crop Protection Council, Farnham (UK). Compound [35] (orthosulfamuron) is described in international patent application WO 98/40361.

15 As already mentioned, the use of the herbicidal compositions, object of the present invention, is particularly advantageous with respect to the use of the single components [A] and [B] as, in addition to having a wider action range, reduced dosages of the products can be
20 adopted for obtaining the same herbicidal effect; the compositions according to the present invention are effective in the post-emergence and pre-emergence control of numerous monocotyledonous and dicotyledonous weeds. At the same time, said compositions have a reduced or zero
25 phytotoxicity with respect to important agricultural

crops thus making their use possible in the selective control of weeds. When required, the compositions can also be used as total herbicides, in relation to the quantity of active principles adopted.

- 5 Examples of weeds which can be effectively controlled using the compositions of the present invention are: Abutilon theophrasti, Adonis spp., Ambrosia spp., Alisma plantago, Amaranthus spp., Amni maius, Anagallis arvensis, Anthemis spp., Aphanes arvensis, Atriplex
- 10 patula, Bidens pilosa, Capsella bursa-pastoris, Chenopodium album, Convolvulus sepium, Datura stramonium, Euphorbia spp., Fumaria officinalis, Galeopsis tetrahit, Galinsoga ciliata, Galium aparine, Geranium spp., Helianthus spp., Ipomea spp., Kochia scoparia, Lamium spp., Ma-
- 15 tricarica spp., Monochoria vaginalis, Myosotis arvensis, Papaver rhoeas, Phaseolus aureus, Polygonum spp., Portulaca oleracea, Raphanus raphanistrum, Rumex crispus, Senecio vulgaris, Sesbania exaltata, Sida spinosa, Sinapis arvensis, Solanum nigrum, Sonchus spp., Stellaria media,
- 20 Thlaspi arvense, Veronica spp., Vicia spp., Viola spp., Xanthium spp., Aegilops tauschii, Alopecurus myosuroides, Apera spp., Avena fatua, Brachiaria spp., Bromus spp., Cenchrus echinatus, Commelina bengalensis, Cynodon dactylon, Cyperus spp., Digitaria spp., Echinocloa spp., Eleu-
- 25 sine indica, Elymus repens, Eragrostis pilosa, Eriochloa

villosa, Fimbristylis spp., Heleocaris avicularis,
Heteranthera spp., Leptochloa spp., Lolium spp., Panicum
spp., Phalaris spp., Poa spp., Scirpus spp., Setaria
viridis, Sorghum spp.

5 Examples of agrarian crops which can be advanta-
geously treated with the compositions of the invention
are: wheat (Triticum sp.), barley (Hordeum vulgare),
maize (Zea mays), soybean (Glycine max), rice (Oryza sa-
tiva), cotton (Gossypium hirsutum), sugarcane (Saccharum
10 officinatum).

In the herbicidal compositions, object of the pres-
ent invention, components [A] and [B] defined above can
be mixed within a very wide ratio, in relation to various
factors such as, for example: the component(s) [B] se-
15 lected, the weeds to be attacked, the degree of infesta-
tion, the climatic conditions, the characteristics of the
soil, the application method.

In general, the ratio between the weight quantity of
component [A] and the weight quantity of the component(s)
20 [B], can vary from 1:0,1 to 1:10,000, preferably from 1:1
to 1:1,000.

For practical use in agriculture, the herbicidal
compositions, object of the present invention, can be ap-
plied in such quantities as to guarantee applicative dos-
25 ages of compound (I) within the range of 0,5-200 g/ha,

preferably 1-100 g/ha, and applicative dosages of the component(s) [B] within the range of 1-10,000 g/ha, preferably 10-5,000 g/ha.

A further object of the present invention relates
5 to a method for the control of weeds in cultivated areas by applying the compositions described above.

For practical use in agriculture, it is often advantageous to adopt the herbicidal compositions, object of the present invention, in the form of suitable formulations which can be already prepared or obtained at the
10 moment of use. This can be effected either by formulating component [A] together with component(s) [B] in the desired ratio, to give the final composition, or by preparing the composition at the moment of use by mixing the
15 relative quantities of component [A] and component(s) [B], formulated separately.

Compositions can be used in the form of dry powders, wettable powders, emulsifying concentrates, micro-emulsions, pastes, granulates, solutions, suspensions,
20 etc.: the choice of the type of composition will depend on the specific use.

The compositions are prepared according to known methods, for example by diluting or dissolving the active substance with a solvent medium and/or solid diluent, optionally in the presence of surface-active agents.
25

Inert solid diluents or supports which can be used are: kaolin, alumina, silica, talc, bentonite, gypsum, quartz, dolomite, attapulgite, montmorillonites, diatomaceous earth, cellulose, starch, etc.

5 Inert liquid diluents which can be used are water, or organic solvents such as aromatic hydrocarbons (xylools, alkylbenzol mixtures, etc.), aliphatic hydrocarbons (hexane, cyclohexane, etc.), halogenated aromatic hydrocarbons (chlorobenzol, etc.), alcohols (methanol, pro-
10 panol, butanol, octanol, etc.), esters (isobutyl acetate, etc.), ketones (acetone, cyclohexanone, acetophenone, isophorone, ethylamylketone, etc.), or vegetable or mineral oils and mixtures thereof, etc.

Surface-active agents which can be used are wetting
15 and emulsifying agents of the non-ionic type (polyethoxylated alkylphenols, polyethoxylated fatty alcohols, etc.), of the anionic type (alkylbenzenesulfonates, alkylsulfonates, etc.), of the cationic type (quaternary salts of alkylammonium, etc.).

20 It is also possible to add dispersing agents (for example lignin and its salts, cellulose derivatives, alginates, etc.), stabilizers (for example antioxidants, ultraviolet-ray absorbers, etc.).

In order to widen the action range of the above compositions, it is possible to add other active ingredients
25

such as, for example, other herbicides, antidotes, fungicides, insecticides, acaricides, fertilizers, etc.

Examples of other herbicides which can be added to the compositions, object of the invention, are:

5 acifluorfen, aclonifen, AKH-7088, ametryn, amicarbazone, amitrole, anilofos, asulam, azafenidin, azimsulfuron, aziprotryne, BAY MKH 6561, benazolin, benfluralin, benfuresate, bensulide, bentazone, benzfendizone, benzobicyclon, benzofenap, benzthiazuron, bifenox, bilanafos, bromacil, bromobutide, bromofenoxim, butachlor, butafenacil,
10 butamifos, butenachlor, butralin, butroxydim, butylate, cafenstrole, carbetamide, carfentrazone-ethyl, chlomethoxyfen, chloramben, chlorbromuron, chlorbufam, chlorflurenol, chloridazon, chlornitrofen, chloroxuron, chlorpropham, chlorthal, chlorthiamid, cinidon ethyl, cinmethylin, cinosulfuron, clethodim, clomeprop, clopyralid, cloransulam-methyl, cumyluron (JC-940), cyanazine, cycloate, cyclosulfamuron, cycloxydim, cyhalofop-butyl, 2,4-D, 2,4-DB, daimuron, dalapon, desmedipham, desmetryn,
15 dicamba, dichlobenil, dichlorprop, dichlorprop-P, diclofop, diclosulam, diethatyl, difenoxuron, difenzoquat, diflufenzopyr, dimefuron, dimepiperate, dimethachlor, dimethametryn, dinitramine, dinoseb, dinoseb acetate, dinoterb, diphenamid, dipropetryn, diquat, dithiopyr, 1-diuron, eglinazine, endothal, EPTC, esprocarb, ethalflu-

25

ralin, ethametsulfuron-methyl, ethidimuron, ethiozin (SMY 1500), ethofumesate, ethoxyfen-ethyl (HC-252), etobenzanid (HW 52), fentrazamide, fenuron, flamprop, flamprop-M, flazasulfuron, florasulam, fluazifop, fluazifop-P, 5 fluazolate (JV 485), flucarbazone-sodium, fluchloralin, flufenpyr ethyl, flumetsulam, flumiclorac-pentyl, flumioxazin, flumipropin, fluoroglycofen, fluoronitrofen, flupoxam, flupropanate, flupyrsulfuron, flurenol, fluridone, flurochloridone, flurtamone, fluthiacet-methyl, fomesafen, foramsulfuron, fosamine, furyloxyfen, haloxyfop, 10 haloxyfop-P-methyl, hexazinone, imazamethabenz, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, indanofan, iodosulfuron, isopropalin, isouron, isoxaben, isoxachlortole, isoxapyrifop, KPP-421, lactofen, lenacil, 15 LS830556, mecoprop, mecoprop-P, mefenacet, mesosulfuron, metamitron, metazachlor, methabenzthiazuron, methazole, methoprotiryne, methyldymron, metobenzuron, metobromuron, metosulam, metoxuron, molinate, monalide, monolinuron, naproanilide, napropamide, naptalam, NC-330, neburon, nicosulfuron, 20 nipyraclufen, norflurazon, orbencarb, oryzalin, oxadiargyl, oxadiazon, oxasulfuron, oxaziclomefone, oxyfluorfen, paraquat, pebulate, pentanochlor, pentoxazone, phenmedipham, picloram, piperophos, preti-lachlor, primisulfuron, prodiamine, profluazol, proglin- 25 azine, prometon, propaquizafop, propazine, propham, pro-

pisochlor, propyzamide, prosulfocarb, prosulfuron, pyra-
clonil, pyraflufen-ethyl, pyrazogyl (HSA-961), pyrazoly-
nate, pyrazosulfuron, pyrazoxyfen, pyribenzoxim, pyribu-
ticarb, pyridafol, pyridate, pyriftalid, pyriminobac-
5 methyl, pyriethiobac-sodium, quinclorac, quinmerac, quiza-
lofop, quizalofop-P, rimsulfuron, sethoxydim, siduron,
simazine, simetryn, sulfentrazone, sulfometuron-methyl,
2,3,6-TBA, TCA-sodium, tebutam, tebuthiuron, tepralox-
dim, terbacil, terbumeton, terbutryn, thenylchlor, thi-
10 azafluron, thiazopyr, thidiazimin, thiobencarb, tiocarpa-
zil, tioclorim, tralkoxydim, triallate, triaziflam,
triclopyr, trietazine, triflusaluron-methyl, tritosulfu-
ron, UBI-C4874, vernolate.

The concentration of active substances [A] + [B],
15 in the above compositions can vary within a wide range,
depending on the active principles selected, the applica-
tions for which they are destined, the environmental con-
ditions and the type of formulation. The overall composi-
tion of active substances can generally range from 1 to
20 90%, preferably from 5 to 75%.

The following examples are provided for a better il-
lustration of the invention.

EXAMPLE 1

Preparation of methyl (E)-4-[2-chloro-5-(4-chloro-5-
25 difluoromethoxy-1-methylpyrazol-3-yl)-4-fluorophenoxy]-3-

methoxybut-2-enoate (component [A])).

14 g (101 mmoles) of potassium carbonate are added to a solution of 32.71 g (100 mmoles) of 4-chloro-3-[4-chloro-2-fluoro-5-hydroxyphenyl]-5-difluoromethoxy-1-methylpyrazole in 300 ml of N,N-dimethyl-formamide (DMF). The mixture is kept under stirring at room temperature for 30 minutes.

A solution of 18 g (109 mmoles) of methyl (E)-4-chloro-3-methoxy-2-butenate in 30 ml of DMF is dripped into the suspension; at the end of the addition, the reaction mixture is heated to 50°C for 4 hours.

At the end of the reaction, the mixture is diluted with water (2 litres) and extracted with methylene chloride (3 x 0.5 litres). The extract is washed to neutrality with water, anhydrified with sodium sulfate; the organic solvent is then removed by distillation under vacuum and the raw product is purified by chromatography on a silica gel column, eluting with hexane/ethyl acetate 65:35. 35 g of a dense oil are obtained, which solidifies after a few days giving a white product with a melting point of 66-69°C.

¹H-NMR (CDCl₃): δ 3,68 (s, 3H); 3,71 (s, 3H); 3,82 (s, 3H); 5,20 (s, 1H); 5,28 (s, 2H); 6,69 (t, 1H); 7,16 (d, 1H aromatic); 7,21 (d, 1H aromatic).

¹⁹F-NMR (CDCl₃): δ a -121,1 (m, 1F); -81,4 (d, 2F).

EXAMPLE 2

a) Determination of the herbicidal activity and phytotoxicity in post-emergence.

The herbicidal activity in post-emergence of the compositions of the invention was evaluated according to the following operating procedures.

The vegetable species of interest (weeds or crops) were planted in vases having an upper diameter of 10 cm, a height of 10 cm and containing sandy earth.

Water was added to each vase in a suitable quantity for the germination of the seeds. The vases were then divided into four groups for each weed or crop.

Fifteen days after planting (ten in the case of wheat), i.e. when the weed seedlings and crops, depending on the species, had reached a height of 10-15 cm, the first group of vases was treated with a hydroacetone dispersion containing acetone at 10% by volume, Tween 20 at 0.5%, and component [A] at a dosage D_A .

The second group was treated with a hydroacetone dispersion containing acetone at 10% by volume, Tween 20 at 0.5%, and component [B] at a dosage D_B .

The third group was treated with a hydroacetone dispersion containing acetone at 10% by volume, Tween 20 at 0.5%, and the composition **C** according to the present invention, containing components [A] and [B] at dosages, D_A

and D_B, respectively.

The fourth group was treated with a hydroacetone solution only, containing acetone at 10% by volume and Tween 20 at 0.5%, and was used as a comparative reference
5 (blank).

All the vases were kept under observation in a conditioned environment under the following environmental conditions:

- temperature: 24°C;
- 10 - relative humidity: 60%;
- photo-period: 16 ore;
- light intensity: 10,000 lux.

Every two days the vases were uniformly watered to ensure a sufficient humidity degree for a good growth of
15 the plants.

Fifteen days after treatment, the herbicidal activity was evaluated (expressed as a % of the damage observed on the vegetable species) for the composition C (E_C) and for the two components [A] and [B] tested separately (E_A, E_B).
20

Weeds tested were: *Abutilon theophrasti*, *Amaranthus retroflexus*, *Amni maius*, *Capsella bursa pastoris*, *Chenopodium album*, *Convolvulus sepium*, *Galium aparine*, *Geranium dissectum*, *Ipomea purpurea*, *Matricaria chamomilla*,
25 *Papaver rhoeas*, *Polygonum persicaria*, *Portulaca oleracea*,

Sida spinosa, Stellaria media, Veronica persica, Viola arvensis, Xanthium italicum, Alopecurus myosuroides, Avena fatua, Digitaria sanguinalis, Echinochloa crus galli, Panicum dicotomiflorum, Setaria viridis, Sorghum
5 halepense.

Crops tested were: wheat, barley, maize, soybean, rice, cotton.

b) Determination of the herbicidal activity and phytotoxicity in pre-emergence.

10 The herbicidal activity in pre-emergence of the compounds of the invention was evaluated according to the following operating procedures.

The vegetable species of interest (weeds or crops) were planted in vases having an upper diameter of 10 cm,
15 a height of 10 cm and containing sandy earth.

Water was added to each vase in a suitable quantity for the germination of the seeds. The vases were then divided into four groups for each weed or crop.

One day after planting, the first group of vases was
20 treated with a hydroacetone dispersion containing acetone at 10% by volume, Tween 20 at 0.5%, and component [A] at a dosage D_A .

The second group was treated with a hydroacetone dispersion containing acetone at 10% by volume, Tween 20
25 at 0.5%, and component [B] at a dosage D_B .

The third group was treated with a hydroacetone dispersion containing acetone at 10% by volume, Tween 20 at 0.5%, and the composition **C** according to the present invention, containing components [A] and [B] at dosages, D_A e D_B , respectively.

The fourth group was treated with a hydroacetone solution only, containing acetone at 10% by volume and Tween 20 at 0.5%, and was used as a comparative reference (blank).

All the vases were kept under observation in a conditioned environment under the following environmental conditions:

- temperature: 24°C;
- relative humidity: 60%;
- photo-period: 16 ore;
- light intensity: 10,000 lux.

Every two days the vases were uniformly watered to ensure a sufficient humidity degree for a good growth of the plants.

Four weeks after treatment, the herbicidal activity was evaluated (expressed as a % of the damage observed on the vegetable species) for the composition (E_C) and for the two components [A] and [B] tested separately (E_A , E_B).

Weeds tested were: *Abutilon theophrasti*, *Amaranthus*

retroflexus, Amni maius, Capsella bursa pastoris, Chenopodium album, Convolvulus sepium, Galium aparine, Geranium dissectum, Ipomea purpurea, Matricaria chamomilla, Papaver rhoeas, Polygonum persicaria, Portulaca oleracea, Sida spinosa, Stellaria media, Veronica persica, Viola arvensis, Xanthium italicum, Alopecurus myosuroides, Avena fatua, Digitaria sanguinalis, Echinochloa crus galli, Panicum dicothomiflorum, Setaria viridis, Sorghum halepense.

Crops tested were: wheat, barley, maize, soybean, rice, cotton.

For both the post-emergence and pre-emergence treatment, a synergistic effect was observed each time the experimental herbicidal activity of the composition, E_c , proved to be higher than that calculated applying the Colby formula ("Weeds", 15 (1967), pages 20-22):

$$E_{\text{teor}} = E_A + E_B - E_A \times E_B / 100$$

wherein:

E_{teor} = activity calculated for the composition consisting of [A] at a dosage D_A + [B] at a dosage D_B ;
 E_A = activity observed for [A] at a dosage D_A ;
 E_B = activity observed for [B] at a dosage D_B .

In Table are reported the compositions for which a remarkable synergistic effect ($E_c/E_{\text{teor}} > 1,10$) against some important weeds in post-emergence or pre-emergence

treatments, was observed.

Table

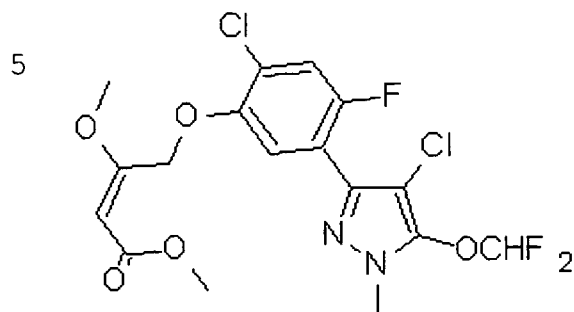
COMPOSITION	COMPONENTS [A]+[B] (TYPE OF APPLICATION)	Rates g ai/ha	
		[A]	[B]
C1	[A] + acetochlor (PRE)	50	900
C2	[A] + alachlor (PRE)	50	760
C3	[A] + amidosulfuron (POST)	10	10
C4	[A] + atrazine (PRE)	50	760
C5	[A] + beflubutamid (POST)	12.5	85
C6	[A] + bensulfuron (POST)	15	30
C7	[A] + bispyribac-Na (POST)	15	25
C8	[A] + bromoxynil (POST)	15	105
C9	[A] + chlorimuron (POST)	15	10
C10	[A] + chlorotoluron (POST)	15	750
C11	[A] + chlorsulfuron (PRE)	40	13
C12	[A] + clodinafop (POST)	12.5	30
C13	[A] + clomazone (POST)	15	150
C14	[A] + diflufenican (POST)	12.5	75
C15	[A] + dimethenamid (PRE)	75	360
C16	[A] + diuron (PRE)	100	750
C17	[A] + ethoxysulfuron (POST)	15	30
C18	[A] + fenoxaprop (POST))	20	35
C19	[A] + flufenacet (PRE)	40	40
C20	[A] + fluometuron (POST)	15	560

C21	[A] + fluroxypyr (POST)	15	500
C22	[A] + glufosinate (PRE)	75	230
C23	[A] + glyphosate (PRE)	100	360
C24	[A] + halosulfuron (POST)	12.5	35
C25	[A] + imazamox (POST)	12.5	17
C26	[A] + ioxynil (POST)	15	125
C27	[A] + isoproturon (PRE)	50	750
C28	[A] + isoxaflutole (PRE)	50	30
C29	[A] + linuron (PRE)	50	300
C30	[A] + MCPA (POST)	15	250
C31	[A] + MCPB (POST)	15	500
C32	[A] + mesotrione (PRE)	50	75
C33	[A] + metolachlor (PRE)	75	900
C34	[A] + S-metolachlor (PRE)	75	480
C35	[A] + metribuzin (PRE)	40	100
C36	[A] + metsulfuron (POST)	12.5	2
C37	[A] + MSMA (POST)	15	1400
C38	[A] + orthosulfamuron (POST)	12.5	37.5
C39	[A] + pendimethalin (PRE)	40	650
C40	[A] + penoxsulam (POST)	12.5	20
C41	[A] + pethoxamid (PRE)	100	600
C42	[A] + picolinafen (POST)	12.5	37.5
C43	[A] + pinoxaden (POST)	25	35
C44	[A] + prometryn (PRE)	50	500

C45	[A] + propachlor (PRE)	40	1600
C46	[A] + propanil (POST)	20	1800
C47	[A] + propoxycarbazone (POST)	12.5	21
C48	[A] + sulcotrione (PRE)	50	150
C49	[A] + sulfosulfuron (POST)	12.5	12.5
C50	[A] + terbuthylazine (PRE)	50	500
C51	[A] + thifensulfuron (POST)	12.5	5
C52	[A]+ triasulfuron (POST)	12.5	5
C53	[A] + tribenuron (POST)	12.5	7.5
C54	[A] + trifloxysulfuron (POST)	15	5
C55	[A] + trifluralin (PRE)	50	140

CLAIMS

1. Synergistic herbicidal compositions comprising a component [A] and a component [B], wherein the component [A] is the compound having formula (I)



(I)

methyl (E)-4-[2-chloro-5-(4-chloro-5-difluoro-methoxy-1-methylpyrazol-3-yl)-4-fluorophenoxy]-3-methoxy-but-2-enoate, and component [B] consists of at least one product selected from the following herbicides:

- 15 [1] acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide);
- [2] alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide);
- [3] amidosulfuron (N-[[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]-N-methylmethanesulfon-
- 20 amide);
- [4] atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine);
- [5] beflubutamid (2-[4-fluoro-3-(trifluoromethyl)-phenoxy]-N-(phenylmethyl)butanamide);
- 25

- [6] bensulfuron-methyl (methyl [[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]-benzoate);
- [7] bispyribac-sodium (sodium 2,6-bis[(4,6-dimethoxy-2-pyrimidinyl)oxy]benzoate);
- [8] bromoxynil (3,5-dibromo-4-hydroxybenzonitrile);
- [9] chlorimuron-ethyl (ethyl [[[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate;
- [10] chlorotoluron (N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea);
- [11] chlorsulfuron (2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide);
- [12] clodinafop-propargyl (propynyl (R)-2-[4-[(5-chloro-3-fluoro-2-pyridinyl)oxy]phenoxy]propanoate);
- [13] clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone);
- [14] diflufenican (N-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridinecarboxamide);
- [15] dimethenamid ((RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide);
- [16] diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea);
- [17] ethoxysulfuron (1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethoxyphenoxy)urea);
- [18] fenoxaprop-P ((R)-2-[4-[(6-chloro-2-benzoxazolyl)-oxy]phenoxy]propanoic acid) and its ethyl ester;

- [19] flufenacet (N-(4-fluorophenyl)-N-(1-methylethyl)-2-
[[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy]-
acetamide);
- [20] fluometuron (N,N-dimethyl-N'-[3-(trifluoromethyl)-
5 phenyl]urea;
- [21] fluroxypyr ([4(4-amino-3,5-dichloro-6-fluoro-2-
pyridinyl)oxy]acetic acid);
- [22] glufosinate (ammonium ($\pm$)-2-amino-4-(hydroxymethyl-
phosphinyl)butanoate);
- 10 [23] glyphosate (N-(phosphonomethyl)glycine) and its
salts;
- [24] halosulfuron (3-chloro-5-[[[(4,6-dimethoxy-2-
pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-
pyrazole-4-carboxylic acid) and its methyl ester;
- 15 [25] imazamox (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-
5-oxo-1H-imidazol-2-yl]-5-(methoxymethyl)-3-
pyridinecarboxylic acid;
- [26] ioxynil (4-hydroxy-3,5-diiodobenzonitrile);
- [27] isoproturon (N,N-dimethyl-N'-[4-(1-methylethyl)-
20 phenyl]urea);
- [28] isoxaflutole ((5-cyclopropyl-4-isoxazolyl)-[2-
(methylsulfonyl)-4-(trifluoromethyl)phenyl]methanone);
- [29] linuron (N'-(3,4-dichlorophenyl)-N-methoxy-N-methyl-
urea);
- 25 [30] MCPA ((4-chloro-2-methylphenoxy)acetic acid) and its

thioethyl ester;

[31] MCPB (4-(4-chloro-2-methylphenoxy)butanoic acid);

[32] mesotrione (2-[4-(methylsulfonyl)-2-nitrobenzoyl]-1,3-cyclohexandione);

5 [33] metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide);

[34] S-metolachlor (mixture of two enantiomers of metolachlor, containing 80-100% of 2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]-

10 acetamide);

[35] metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one);

[36] metsulfuron-methyl (methyl 2-[[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]-

15 sulfonyl]-benzoate);

[37] MSMA (monosodium methyl arsonate);

[38] orthosulfamuron (2-[[[[(4,6-dimethoxy-2-pyrimidin-yl)amino]carbonyl]amino]sulfonyl]amino-N,N-dimethylbenzamide);

20 [39] pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine);

[40] penoxsulam (2-(2,2-difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide);

25 [41] pethoxamid (2-chloro-N-(2-ethoxyethyl)-N-(2-methyl-

1-phenyl-1-propenyl)acetamide);

[42] picolinafen (N-(4-fluorophenyl)-6-[3-(trifluoromethyl)phenoxy]-2-pyridinecarboxamide);

[43] pinoxaden (8-(2,6-diethyl-4-methylphenyl)-1,2,4,5-tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropanoate);

[44] prometryn (N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine;

[45] propachlor (2-chloro-N-(methylethyl)-N-phenylacetamide);

[46] propanil (N-(3,4-dichlorophenyl)propanamide);

[47] propoxycarbazone (methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1H-1,2,4-triazol-1-yl)carbonyl]amino]-sulfonyl]benzoate);

[48] sulcotrione (2-[2-chloro-4-(methylsulfonyl)-benzoyl]-1,3-cyclohexanedione);

[49] sulfosulfuron (N-[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]-2-(ethylsulfonyl)imidazo[1,2-a]pyridin-3-sulfonamide);

[50] terbuthylazine (6-chloro-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine);

[51] thifensulfuron-methyl (methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate);

[52] triasulfuron (2-(2-chloroethoxy)-N-[[[(4-methoxy-6-

methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide);

[53] tribenuron-methyl (methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]-sulfonyl]benzoate);

[54] trifloxysulfuron (N-[[[(4,6-dimethoxy-2-pyrimidin-2-yl)amino]carbonyl]-3-(2,2,2-trifluoroethoxy)-2-pyridine-sulfonamide);

[55] trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzeneamine).

2. The synergistic herbicidal compositions according to claim 1, characterized in that component [B] is selected from bromoxynil, diflufenican, flufenacet, glyphosate, ioxynil, isoproturon, mesotrione, S-metolachlor.

3. The synergistic herbicidal compositions according to claim 1, characterized in that the weight quantity of component [A] is such as to ensure applicative dosages of the compound (I) ranging from 0,5 to 200 g/ha.

4. The synergistic herbicidal compositions according to claim 3, characterized in that the applicative dosages of the compound (I) range from 1 to 100 g/ha.

5. The synergistic herbicidal compositions according to claim 1, characterized in that the applicative dosages of the component(s) [B] range from 1 to 10,000 g/ha.

6. The synergistic herbicidal compositions according to

claim 5, characterized in that the applicative dosages of the component(s) [B] range from 10 to 5,000 g/ha.

7. The synergistic herbicidal compositions according to claim 1, characterized in that weight ratio between the quantity of component [A] and the quantity of component(s) [B] ranges from 1:0.1 to 1:10,000.

8. The synergistic herbicidal compositions according to claim 7, characterized in that the weight ratio ranges from 1:1 to 1:1,000.

9. The synergistic herbicidal compositions according to claim 1, characterized in that they consist of formulations in the form of dry powders, wettable powders, emulsifying concentrates, micro-emulsions, pastes, granulates, solutions, suspensions.

10. The synergistic herbicidal compositions according to claim 9, characterized in that they consist of formulations already prepared containing component [A] and component(s) [B], in the desired ratio, or obtained at the moment of use by mixing the relative quantities of component [A] and component(s) [B], formulated separately.

11. The synergistic herbicidal compositions according to claim 1, characterized in that they also contain further active substances such as, for example, other herbicides, antidotes, fungicides, insecticides, acaricides, fertilizers, etc.

12. The synergistic herbicidal compositions according to claim 11, characterized in that the further herbicides are selected from:

acifluorfen, aclonifen, AKH-7088, ametryn, amicarbazone,
5 amitrole, anilofos, asulam, azafenidin, azimsulfuron,
aziprotryne, BAY MKH 6561, benazolin, benfluralin, ben-
furesate, bensulide, bentazone, benzfendizone, benzobicy-
clon, benzofenap, benzthiazuron, bifenox, bilanafos, bro-
macil, bromobutide, bromofenoxim, butachlor, butafenacil,
10 butamifos, butenachlor, butralin, butroxydim, butylate,
cafenstrole, carbetamide, carfentrazone-ethyl, chlometh-
oxyfen, chloramben, chlorbromuron, chlorbufam, chlor-
flurenol, chloridazon, chlornitrofen, chloroxuron, chlor-
propham, chlorthal, chlorthiamid, cinidon ethyl, cinmeth-
15 ylin, cinosulfuron, clethodim, clomeprop, clopyralid,
cloransulam-methyl, cumyluron (JC-940), cyanazine, cy-
cloate, cyclosulfamuron, cycloxydim, cyhalofop-butyl,
2,4-D, 2,4-DB, daimuron, dalapon, desmedipham, desmetryn,
dicamba, dichlobenil, dichlorprop, dichlorprop-P, diclo-
20 fop, diclosulam, diethatyl, difenoxuron, difenzoquat, di-
flufenzopyr, dimefuron, dimepiperate, dimethachlor, di-
methametryn, dinitramine, dinoseb, dinoseb acetate, di-
noterb, diphenamid, dipropetryn, diquat, dithiopyr, 1-
diuron, eglinazine, endothal, EPTC, esprocarb, ethalflu-
25 ralin, ethametsulfuron-methyl, ethidimuron, ethiozin (SMY

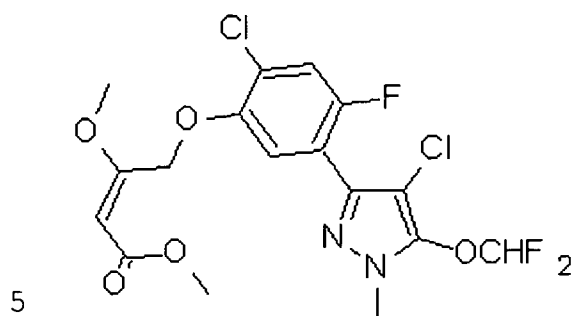
1500), ethofumesate, ethoxyfen-ethyl (HC-252), etobenza-
nid (HW 52), fentrazamide, fenuron, flamprop, flamprop-M,
flazasulfuron, florasulam, fluazifop, fluazifop-P,
fluazolate (JV 485), flucarbazone-sodium, fluchloralin,
5 flufenpyr ethyl, flumetsulam, flumiclorac-pentyl, flumi-
oxazin, flumipropin, fluoroglycofen, fluoronitrofen, flu-
poxam, flupropanate, flupyrsulfuron, flurenol, fluridone,
flurochloridone, flurtamone, fluthiacet-methyl, fome-
safen, foramsulfuron, fosamine, furyloxyfen, haloxyfop,
10 haloxyfop-P-methyl, hexazinone, imazamethabenz, imazapic,
imazapyr, imazaquin, imazethapyr, imazosulfuron, indano-
fan, iodosulfuron, isopropalin, isouron, isoxaben, isoxa-
chlortole, isoxapyrifop, KPP-421, lactofen, lenacil,
LS830556, mecoprop, mecoprop-P, mefenacet, mesosulfuron,
15 metamitron, metazachlor, methabenzthiazuron, methazole,
methoprottryne, methyldymron, metobenzuron, metobromuron,
metosulam, metoxuron, molinate, monalide, monolinuron,
naproanilide, napropamide, naptalam, NC-330, neburon, ni-
cosulfuron, nipyraclufen, norflurazon, orbencarb,
20 oryzalin, oxadiargyl, oxadiazon, oxasulfuron, oxaziclome-
fone, oxyfluorfen, paraquat, pebulate, pentanochlor, pen-
toxazone, phenmedipham, picloram, piperophos, preti-
lachlor, primisulfuron, prodiamine, profluazol, proglin-
azine, prometon, propaquizafop, propazine, propham, pro-
25 pisochlor, propyzamide, prosulfocarb, prosulfuron, pyra-

clonil, pyraflufen-ethyl, pyrazogyl (HSA-961), pyrazolynate, pyrazosulfuron, pyrazoxyfen, pyribenzoxim, pyributicarb, pyridafol, pyridate, pyriftalid, pyriminobacmethyl, pyriothiobac-sodium, quinclorac, quinmerac, quizalofop, quizalofop-P, rimsulfuron, sethoxydim, siduron, simazine, simetryn, sulfentrazone, sulfometuron-methyl, 2,3,6-TBA, TCA-sodium, tebutam, tebuthiuron, tepraloxymdim, terbacil, terbumeton, terbutryn, thenylchlor, thiazafururon, thiazopyr, thidiazimin, thiobencarb, tiocarbazil, tioclorim, tralkoxydim, triallate, triaziflam, triclopyr, trietazine, triflusulfuron-methyl, tritosulfuron, UBI-C4874, vernolate.

13. The synergistic herbicidal compositions according to claim 11, characterized in that the concentration of active substances, also comprising [A] + [B], ranges from 1 to 90%.

14. The synergic herbicidal compositions according to claim 13, characterized in that the concentration ranges from 5 to 75%.

15. Use of synergistic herbicidal compositions comprising a component [A] and a component [B], wherein the component [A] is the compound having formula (I)



(I)

methyl (*E*)-4-[2-chloro-5-(4-chloro-5-difluoro-methoxy-1-methylpyrazol-3-yl)-4-fluorophenoxy]-3-methoxy-but-2-enoate, and component [B] consists of at least one product selected from the following herbicides:

10

[1] acetochlor (2-chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide);

[2] alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide);

15 [3] amidosulfuron (N-[[[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]amino]sulfonyl]-N-methylmethanesulfonamide);

[4] atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine);

20 [5] beflubutamid (2-[4-fluoro-3-(trifluoromethyl)-phenoxy]-N-(phenylmethyl)butanamide);

[6] bensulfuron-methyl (methyl [[[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]methyl]-benzoate);

25 [7] bispyribac-sodium (sodium 2,6-bis[(4,6-dimethoxy-2-

- pyrimidinyl)oxy]benzoate);
- [8] bromoxynil (3,5-dibromo-4-hydroxybenzonitrile);
- [9] chlorimuron-ethyl (ethyl [[(4-chloro-6-methoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]benzoate;
- 5 [10] chlorotoluron (N'-(3-chloro-4-methylphenyl)-N,N-dimethylurea);
- [11] chlorsulfuron (2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide);
- [12] clodinafop-propargyl (propynyl (R)-2-[4-[(5-chloro-10 3-fluoro-2-pyridinyl)oxy]phenoxy]propanoate);
- [13] clomazone (2-[(2-chlorophenyl)methyl]-4,4-dimethyl-3-isoxazolidinone);
- [14] diflufenican (N-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]-3-pyridinecarboxamide);
- 15 [15] dimethenamid ((RS)-2-chloro-N-(2,4-dimethyl-3-thienyl)-N-(2-methoxy-1-methylethyl)acetamide);
- [16] diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea);
- [17] ethoxysulfuron (1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethoxyphenoxy)sulfonyl)urea);
- 20 [18] fenoxaprop-P ((R)-2-[4-[(6-chloro-2-benzoxazolyl)-oxy]phenoxy]propanoic acid) and its ethyl ester;
- [19] flufenacet (N-(4-fluorophenyl)-N-(1-methylethyl)-2-[[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy]-acetamide);
- 25 [20] fluometuron (N,N-dimethyl-N'-[3-(trifluoromethyl)-

phenyl]urea;

[21] fluroxypyr ([4(4-amino-3,5-dichloro-6-fluoro-2-pyridinyl)oxy]acetic acid);

[22] glufosinate (ammonium ($\pm$)-2-amino-4-(hydroxymethyl-
5 phosphinyl)butanoate);

[23] glyphosate (N-(phosphonomethyl)glycine) and its salts;

[24] halosulfuron (3-chloro-5-[[[(4,6-dimethoxy-2-pyrimidinyl)amino]carbonyl]amino]sulfonyl]-1-methyl-1H-
10 pyrazole-4-carboxylic acid) and its methyl ester;

[25] imazamox (2-[4,5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo-1H-imidazol-2-yl]-5-(methoxymethyl)-3-pyridinecarboxylic acid);

[26] ioxynil (4-hydroxy-3,5-diiodobenzonitrile);

[27] isoproturon (N,N-dimethyl-N'-[4-(1-methylethyl)-phenyl]urea);

[28] isoxaflutole ((5-cyclopropyl-4-isoxazolyl)-[2-(methylsulfonyl)-4-(trifluoromethyl)phenyl]methanone);

[29] linuron (N'-(3,4-dichlorophenyl)-N-methoxy-N-methyl-
20 urea);

[30] MCPA ((4-chloro-2-methylphenoxy)acetic acid) and its thioethyl ester;

[31] MCPB (4-(4-chloro-2-methylphenoxy)butanoic acid);

[32] mesotrione (2-[4-(methylsulfonyl)-2-nitrobenzoyl]-
25 1,3-cyclohexandione);

- [33] metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide);
- [34] S-metolachlor (mixture of two enantiomers of metolachlor, containing 80-100% of 2-chloro-N-(2-ethyl-6-methylphenyl)-N-[(1S)-2-methoxy-1-methylethyl]-acetamide);
- [35] metribuzin (4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4H)-one);
- [36] metsulfuron-methyl (methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]-sulfonyl]-benzoate);
- [37] MSMA (monosodium methyl arsonate);
- [38] orthosulfamuron (2-[[[(4,6-dimethoxy-2-pyrimidin-yl)amino]carbonyl]amino]sulfonyl]amino-N,N-dimethylbenzamide);
- [39] pendimethalin (N-(1-ethylpropyl)-3,4-dimethyl-2,6-dinitrobenzenamine);
- [40] penoxsulam (2-(2,2-difluoroethoxy)-N-(5,8-dimethoxy[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide);
- [41] pethoxamid (2-chloro-N-(2-ethoxyethyl)-N-(2-methyl-1-phenyl-1-propenyl)acetamide);
- [42] picolinafen (N-(4-fluorophenyl)-6-[3-(trifluoromethyl)phenoxy]-2-pyridinecarboxamide);
- [43] pinoxaden (8-(2,6-diethyl-4-methylphenyl)-1,2,4,5-

tetrahydro-7-oxo-7H-pyrazolo[1,2-d][1,4,5]oxadiazepin-9-yl 2,2-dimethylpropanoate);

[44] prometryn (N,N'-bis(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine;

5 [45] propachlor (2-chloro-N-(methylethyl)-N-phenyl-acetamide);

[46] propanil (N-(3,4-dichlorophenyl)propanamide);

[47] propoxycarbazone (methyl 2-[[[(4,5-dihydro-4-methyl-5-oxo-3-propoxy-1H-1,2,4-triazol-1-yl)carbonyl]amino]-
10 sulfonyl]benzoate);

[48] sulcotrione (2-[2-chloro-4-(methylsulfonyl)-benzoyl]-1,3-cyclohexanedione);

[49] sulfosulfuron (N-[[(4,6-dimethoxy-2-pyrimidinyl)-amino]carbonyl]-2-(ethylsulfonyl)imidazo[1,2-a]pyridin-3-
15 sulfonamide);

[50] terbuthylazine (6-chloro-N-(1,1-dimethylethyl)-N'-ethyl-1,3,5-triazine-2,4-diamine);

[51] thifensulfuron-methyl (methyl 3-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]amino]sulfonyl]-
20 2-thiophenecarboxylate);

[52] triasulfuron (2-(2-chloroethoxy)-N-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide);

[53] tribenuron-methyl (methyl 2-[[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)methylamino]carbonyl]amino]-
25

sulfonyl]benzoate);

[54] trifloxysulfuron (N-[[[4,6-dimethoxy-2-pyrimidin-2-yl)amino]carbonyl]-3-(2,2,2-trifluoroethoxy)-2-pyridine-sulfonamide);

5 [55] trifluralin (2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzeneamine)

for the control of weeds in agricultural crops.

16. Use of the synergistic herbicidal compositions according to any of the claims from 2 to 14, for the control of weeds in agricultural crops.

17. Use according to claim 15 or 16 for the control, in both post-emergence and in pre-emergence, of monocotyledonous and dicotyledonous weeds and/or for the treatment of agricultural crops.

15 18. Use according to claim 15 or 16 for the control of Abutilon theophrasti, Adonis spp., Ambrosia spp., Alisma plantago, Amaranthus spp., Amni maius, Anagallis arvensis, Anthemis spp., Aphanes arvensis, Atriplex patula, Bidens pilosa, Capsella bursa-pastoris, Chenopodium album, Convolvulus sepium, Datura stramonium, Euphorbia spp., Fumaria officinalis, Galeopsis tetrahit, Galinsoga ciliata, Galium aparine, Geranium spp., Helianthus spp., Ipomea spp., Kochia scoparia, Lamium spp., Matricaria spp., Monochoria vaginalis, Myosotis arvensis, Papaver
20 rhoeas, Phaseolus aureus, Polygonum spp., Portulaca ol-
25

eracea, Raphanus raphanistrum, Rumex crispus, Senecio vulgaris, Sesbania exaltata, Sida spinosa, Sinapis arvensis, Solanum nigrum, Sonchus spp., Stellaria media, Thlaspi arvense, Veronica spp., Vicia spp., Viola spp.,
 5 Xanthium spp., Aegilops tauschii, Alopecurus myosuroides, Apera spp., Avena fatua, Brachiaria spp., Bromus spp., Cenchrus echinatus, Commelina bengalensis, Cynodon dactylon, Cyperus spp., Digitaria spp., Echinocloa spp., Eleusine indica, Elymus repens, Eragrostis pilosa, Eriochloa
 10 villosa, Fimbristylis spp., Heleocaris avicularis, Heteranthera spp., Leptochloa spp., Lolium spp., Panicum spp., Phalaris spp., Poa spp., Scirpus spp., Setaria viridis, Sorghum spp..

19. Use according to claim 15 or 16 for the treatment of
 15 wheat (Triticum sp.), barely (Hordeum vulgare), maize (Zea mays), soybean (Glycine max), rice (Oryza sativa), cotton (Gossypium hirsutum), sugarcane (Saccharum officinarum).

20. A method for the control of weeds in cultivated areas by means of the application of synergistic herbicidal compositions according to any of the claims from 1 to 14.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/001706

A. CLASSIFICATION OF SUBJECT MATTER

INV. A01N43/56	A01P13/00	A01N33/18	A01N37/20	A01N37/22
A01N37/26	A01N37/40	A01N39/02	A01N39/04	A01N41/10
A01N43/10	A01N43/40	A01N43/50	A01N43/54	A01N43/70

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A01N

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 1 020 448 A2 (ISAGRO RICERCA SRL [IT]) 19 July 2000 (2000-07-19) cited in the application paragraphs [0004], [0005], [0016] - [0020], [0031]; example 2	1-20
Y	EP 0 619 946 A1 (NIHON NOHYAKU CO LTD [JP]) 19 October 1994 (1994-10-19) page 2, lines 5-25 page 3; table 1 page 4, line 1 - page 6, line 25 Test example 1 and tables 5 - 7	1-20
Y	EP 0 595 126 A1 (NIHON NOHYAKU CO LTD [JP]) 4 May 1994 (1994-05-04) page 3, lines 5-51 Test example 1, tables 2 and 3	1-20
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

27 June 2007

Date of mailing of the international search report

17/07/2007

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2007/001706

C(Continuation). 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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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/001706

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		DE 69333848 T2	12-01-2006
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DE 19859224	A1	06-05-1999 NONE	