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Benævnelse: Selettive herbicider på basis af heteroaryloxy-acetamider

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WO-A-96/11575
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Description

The invention relates to novel selective-herbicidal synergistic active compound combinations comprising a known heteroaryloxy-acetamide and a known herbicidally active compound and optionally compounds which improve crop plant tolerance, which active compound combinations can be used with particularly good results for the selective control of weeds in crops of various useful plants.


Surprisingly, it has now been found that a known active compound from the group of the heteroaryloxy-acetamides, when used together with a known herbicidally active compound and optionally compounds which improve crop plant tolerance, shows pronounced synergistic effects with respect to the action against weeds and/or have significantly improved crop plant tolerance and can be used particularly advantageously as a broad-spectrum combination preparation for the selective
control of weeds in crops of useful plants, such as, for example, in cotton, barley, maize, potatoes, oilseed rape, rice, soya beans, sunflowers, wheat and sugar cane.

5 The invention provides selective herbicidal compositions, characterized in that they comprise an effective amount of an active compound combination consisting of

(a) compound N-i-propyl-N-(4-fluoro-phenyl)-α-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl-oxy)-acetamide (flufenacet)

("active compound of group 1") and

(b) the compound N-(4,6-dimethoxypyrimidin-2-yl)-N’-(3-methoxycarbonyl-6-trifluoromethylpyridin-2-ylsulphonyl)urea, sodium salt (flupyrdsulfuron-methyl-sodium)

("active compound of group 2")

and, if appropriate, additionally

(c) a compound which improves crop plant tolerance, from amongst the following group of compounds:

25 4-dichloroacetyl-1-oxa-4-aza-spiro[4.5]-decane (AD-67), 1-dichloroacetyl-hexahydro-3,3,8a-trimethylpyrrollo[1,2-a]-pyrimidin-6(2H)-one (dicyclonon, BAS-145138), 4-dichloroacetyl-3,4-dihydro-3-methyl-2H-1,4-benzoxazine (benoxacor), 1-methyl-hexyl 5-chloro-quinoline-8-oxy-acetate (cloquintocet-mexyl), α-(cyanomethoximino)-phenylacetonitrile (cyometrinil), 2,2-dichloro-N-(2-oxo-2-(2-propenylamino)-ethyl)-N’-(2-propenyl)-acetamide (DKA-24), 2,2-dichloro-N,N-di-2-propenyl-acetamide (dichlorimid), N-(4-methyl-phenyl)-N’-(1-methyl-1-phenyl-ethyl)-urea (dymron), 4,6-dichloro-2-phenyl-pyrimidine (fenclorim), ethyl 1-(2,4-dichloro-phenyl)-5-trichloromethyl-1H-1,2,4-triazole-3-carboxylate (fenchlorazol-ethyl), phenylmethyl 2-chloro-4-trifluoromethyl-thiazole-5-carboxylate (flurazole), 4-chloro-N-(1,3-dioxolan-2-yl-
methoxy)-α-trifluoro-acetophenone oxime (fluxofenim), 3-dichloroacetyl-5-(2-furanyl)-2,2-dimethyl-oxazolidine (furilazole, MON-13900), ethyl 4,5-dihydro-5,5-diphenyl-3-isoxazolecarboxylate (isoxadifen-ethyl), diethyl-1-(2,4-dichlorophenyl)-4,5-dihydro-5-methyl-1H-pyrazole-3,5-dicarboxylate (mefenpyr-diethyl), 2-dichloromethyl-2-methyl-1,3-dioxolane (MG-191), 1,8-naphthalenedicarboxylic anhydride, α-(1,3-dioxolan-2-yl-methoximino)-phenylacetonitrile (oxabetrinil), 2,2-dichloro-N-(1,3-dioxolan-2-yl-methyl)-N-(2-propenyl)-acetamide (PPG-1292), 3-dichloroacetyl-2,2-dimethyl-oxazolidine (R-28725), 3-dichloroacetyl-2,2,5-trimethyl-oxazolidine (R-29148), methyl 1-(2-chloro-phenyl)-5-phenyl-1H-pyrazole-3-carboxylate and N-(2-methoxy-benzoyl)-4-[(methylamino-carbonyl)-amino]-benzenesulphonamide

("active compounds of group 3").

The active compound of group 1 is described in the patent applications or patents mentioned above.

According to its chemical structure, the active compound of group 2 can be assigned to the following class of active compounds:

Sulphonylureas (e.g. azimsulfuron, flupyrsulfuron-methyl-sodium, foramsulfuron, iodosulfuron-methyl-sodium, mesosulfuron, trifluoxysulfuron, triflusulfuron-methyl).

In particular, the compositions according to the invention comprise the active compound of group 1, the active compound of group 2 and optionally one active compound of group 3.

Surprisingly, it has now been found that the above-defined active compound combinations of heteroaryloxy-acetamide and the active compound of group 2 exhibit a particularly high herbicidal activity combined with very good crop plant compatibility and can be used for the selective control of monocotyledonous and dicotyledonous weeds in a variety of
crops, in particular in barley, potatoes, maize, rice, soya beans and wheat, and additionally also for controlling monocotyledonous and dicotyledonous weeds in the semi- and non-selective field.

Surprisingly, the herbicidal activity of the active compound combinations according to the invention exceeds the total of the actions of the individual active compounds considerably.

Thus, not just a complementation of actions but a synergistic effect is present which could not have been predicted. The novel active compound combinations are well tolerated in a variety of crops, also effecting good control of weeds which are otherwise difficult to control. Thus, the novel active compound combinations are a valuable addition to the herbicides.

The synergistic effect of the active compound combinations according to the invention is particularly strongly pronounced in certain concentration ratios. However, the weight ratios of the active compounds in the active compound combinations may be varied within relatively wide ranges. In general, from 0.01 to 1000 parts by weight, preferably from 0.02 to 500 parts by weight and particularly preferably from 0.05 to 100 parts by weight of active compound of group 2 are used per part by weight of active compound of group 1.

The following may be particularly emphasized as mixing components from amongst the active compounds of group 3:

1-methyl-hexyl 5-chloro-quinoline-8-oxy-acetate (cloquintocet-mexyl), ethyl 4,5-dihydro-5,5-diphenyl-3-isoxazolecarboxylate (isoxadifen-ethyl) and diethyl-1-((2,4-dichloro-phenyl)-4,5-dihydro-5-methyl-1H-pyrazole-3,5-dicarboxylate (mefenpyr-diethyl) to improve tolerance in cereals, and 4-dichloroacetyl-1-oxa-4-aza-spiro[4.5]-decane (AD-67), 1-dichloroacetyl-hexahydro-3,3,8a-trimethylpyrrolo[1,2-a]-pyrimidin-6(2H)-one (BAS-145138), 4-dichloroacetyl-3,4-dihydro-3-methyl-
2H-1,4-benzoxazine (benoxacor), 2,2-dichloro-N,N-di-2-propenyl-acetamide (dichlormid), 2,2-dichloro-N-(2-oxo-2-(2-propenylamino)-ethyl)-N-(2-propenyl)-acetamide (DKA-24), 3-dichloroacetyl-5-(2-furanyl)-2,2-dimethyl-oxazolidine (furilazole, MON-13900), 3-dichloroacetyl-2,2,5-trimethyl-oxazolidine (R-29148) to improve tolerance in maize.

Examples of active compound combinations according to the invention - optionally also including safeners - which may be mentioned are:

flufenacet + flupyrsulfuron-methyl-sodium, flufenacet + flupyrsulfuron-methyl-sodium + mepfynpyr-dietethyl, flufenacet + flupyrsulfuron-methyl-sodium + cloquintocet-mexyl.

It must be considered as surprising that, from amongst a large number of known safeners or antidotes capable of antagonizing the harmful effect of a herbicide on the crop plants, it is precisely the abovementioned compounds of group 3 which are capable of almost completely compensating the harmful effect, on the crop plants, of the active compound of group 1 and its salts, if appropriate also in combination with the abovementioned active compound of group 2, without adversely affecting the herbicidal efficacy towards the weeds.

Even without addition of an active compound of group 2, the following active compounds of group 3 have been found to be highly suitable according to the invention for improving the crop plant compatibility of the active compounds of group 1:

1-dichloroacetyl-hexahydro-3,3,8a-trimethylpyrrolo[1,2-a]-pyrimidin-6(2H)-one (dicyclonon, BAS-145138), ethyl 4,5-dihydro-5,5-diphenyl-3-isoxazolcarboxylate (isoxadifien-ethyl), diethyl 1-(2,4-dichlorophenyl)-4,5-dihydro-5-methyl-1H-pyrazole-3,5-dicarboxylate (mefenpyr-dietethyl), 3-dichloroacetyl-2,2-dimethyl-oxazolidine (R-28725), 3-dichloroacetyl-2,2,5-trimethyl-oxazolidine (R-29148) and methyl 1-(2-chlorophenyl)-5-phenyl-1H-pyrazole-3-carboxylate.
The advantageous effect of the crop plant compatibility of the active compound combinations according to the invention is likewise particularly strongly pronounced at certain concentration ratios. However, the weight ratios of the active compounds in the active compound combinations may be varied within relatively wide ranges. In general, from 0.001 to 1000 parts by weight, preferably from 0.01 to 100 parts by weight and particularly preferably from 0.1 to 10 parts by weight of active compound(s) of group 3 are used per part by weight of the active compound of group 1 or its mixtures with the active compound of group 2.

All plants and plant parts can be treated in accordance with the invention. Plants are to be understood as meaning in the present context all plants and plant populations such as desired and undesired wild plants or crop plants (inclusive of naturally occurring crop plants). Crop plants can be plants which can be obtained by conventional plant breeding and optimization methods or by biotechnological and recombinant methods or by combinations of these methods, inclusive of the transgenic plants and inclusive of the plant varieties protecetable or not protecetable by plant breeders’ rights. Plant parts are to be understood as meaning all aerial and subterranean plant parts and organs of the plants such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stalks, trunks, flowers, fruiting bodies, fruits, seeds, roots, tubers and rhizomes. The plant parts also include vegetative and generative propagation material, for example cuttings, tubers, rhizomes, seedlings and seeds.

The treatment according to the invention, of the plant and plant parts with the active compounds is carried out directly or by allowing the compounds to act on the surroundings, environment or storage space by the customary treatment methods, for example by immersion, spraying, evaporation, fogging, scattering, painting on and, in the case of
propagation material, in particular in the case of seeds, also by applying one or more coats.

Amongst the plants obtained by biotechnological and recombinant methods, or by combining these methods, plants which are emphasized are those which tolerate so-called 4-HPPD, EPSP and/or PPO inhibitors, such as, for example, Acuron plants.

The active compounds according to the invention can be used, for example, in the following plants:


dicotyledonous crops of the genera: Arachis, Beta, Brassica, Cucumis, Cucurbita, Helianthus, Daucus, Glycine, Gossypium, Ipomoea, Lactuca, Linum, Lycopersicon, Nicotiana, Phaseolus, Pisum, Solanum, Vicia;


However, the use of the active compound combinations according to the invention is in no way restricted to these genera, but also extends in the same manner to other plants.

The active compound combinations to be used in accordance with the invention can be employed not only in conventional cultivation methods (suitably spaced row crops), in plantation crops (for example grapevines, fruit, citrus) and in industrial plants and railtracks, on paths and squares, but also for stubble treatment and in the minimum tillage method. They are furthermore suitable as dessicants (haulm killing in, for example, potatoes) or as defoliants (for example in cotton). They are furthermore suitable for use on non-crop areas. Other fields of application are nurseries, forests, grassland and the production of ornamentals.

The active compound combinations can be converted into the customary formulations such as solutions, emulsions, wettable powders, suspensions, powders, dusts, pastes, soluble powders, granules, suspo-emulsion concentrates, natural and synthetic materials impregnated with active compound, and microencapsulations in polymeric materials.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is, liquid solvents and/or solid carriers, optionally with the use of surfactants, that is, emulsifiers and/or dispersants and/or foam formers.

If the extender used is water, it is also possible to employ, for example, organic solvents as cosolvents. The following are essentially suitable as liquid solvents: aromatics such as xylene, toluene, or alkynaphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons such as chlorobenzenes,
chloroethylenes or methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulphoxide, or else water.

Solid carriers which are suitable are:

for example ammonium salts and ground natural minerals such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic materials such as highly-dispersed silica, alumina and silicates; suitable solid carriers for granules are for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; suitable emulsifiers and/or foam formers are for example nonionic and anionic emulsifiers such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alky sulphates, arylsulphonates, or else protein hydrolysates; suitable dispersants are for example ligninosulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other possible additives are mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs
and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95 per cent by weight of active compounds, preferably between 0.5 and 90%.

The active compound combinations according to the invention are generally applied in the form of ready mixes. However, the active compounds contained in the active compound combinations may also be applied in the form of individual formulations which are mixed upon use, that is, in the form of tank mixes.

The novel active compound combinations, as such or in their formulations, may furthermore also be used as a mixture with other known herbicides, again with ready mixes or tank mixes being possible. A mixture with other known active compounds such as fungicides, insecticides, acaricides, nematicides, bird repellents, growth substances, plant nutrients and soil conditioners is also possible. It may furthermore be advantageous for specific applications, in particular for the post-emergence method, to incorporate into the formulations plant-compatible mineral or vegetable oils (for example the commercial product “Oleo Dupont 11E”) or ammonium salts such as, for example, ammonium sulphate or ammonium thiocyanate, as further additives.

The novel active compound combinations can be used as such, in the form of their formulations or the use forms which can be prepared from these formulations by further dilution, such as ready-to-use solutions, suspensions, emulsions, powders, pastes and granules. Application is effected in the customary manner, for example by pouring, spraying, atomizing, dusting or broadcasting.

The active compound combinations according to the invention can be applied before and after emergence of the plants, that
is to say by the pre- and post-emergence method. They may also be incorporated into the soil prior to sowing.

A synergistic effect in herbicides is always present when the herbicidal action of the active compound combination exceeds the action of the active compounds when applied individually.

The expected action for a given combination of two herbicides can be calculated as follows (cf. COLBY, S.R.: "Calculating synergistic and antagonistic responses of herbicide combinations", Weeds 15, pages 20-22, 1967):

If

\[ X = \% \text{ damage by herbicide A (active compound of group 1)} \]
\[ \text{at an application rate of p kg/ha} \]
\[ \text{and} \]
\[ Y = \% \text{ damage by herbicide B (active compound of group 2)} \]
\[ \text{at an application rate of q kg/ha} \]

and

\[ E = \text{the expected damage of herbicides A + B at an application rate of p + q kg/ha,} \]

then

\[ E = X + Y - (X \times Y/100). \]

If the actual damage exceeds the calculated value, the combination has a superadditive effect, that is to say a synergistic effect.

The active compound combinations of the present invention do indeed have the property that their actual herbicidal activity is stronger than the calculated activity, i.e. the novel active compound combinations act synergistically.
Patentkrav

1. Middel indeholdende et aktivt indhold af en kombination af aktivstoffer bestående af

(a) forbindelse N-i-propyl-N-(4-fluor-phenyl)-α-(5-trifluormethyl-1,3,4-thiadiazol-2-yl-oxy)-acetamid (flufenacet)
("aktivstof fra gruppe 1") og
(b) af forbindelsen N-(4,6-dimethoxy-pyrimidin-2-yl)-N'-(3-methoxy carbonyl-6-trifluormethyl-pyridin-2-yl-sulfonyl)-carbamid-natriumsalt (flupyr sulfuron-methyl-sodium)
("aktivstof fra gruppe 2")
samt i givet fald endvidere
(c) en forbindelse, der forbedrer kulturplanteforligeligheden,

fra den følgende gruppe af forbindelser:
4-dichloracetyl-1-oxa-4-aza-spiro[4.5]-decan (AD-67), 1-dichloracetyl-hexahydro-3,3,8a-trimethylpyrrolo[1,2-a]-pyrimidin-6(2H)-on (dicyclonon, BAS-145138), 4-dichloracetyl-3,4-dihydro-3-methyl-2H-1,4-benzoxazin (benoxacor), 5-chlorquinolin-8-oxy-2H-eddikesyre-(1-methyl-hexylester) (cloquintocet-mexyl), α-(cyanomethoxyimino)-phenylacetonitril (cyometrinil), 2,2-dichlor-N-(2-oxo-2- (2-propenylamino)-ethyl)-N-(2-propenyl)-acetamid (DKA-24), 2,2-dichlor-N,N-di-2-propenylacetamid (dichlormid), N-(4-methyl-phenyl)-N'-(1-methyl-1-phenyl-ethyl)-carbamid (dymron), 4,6-dichlor-2-phenylpyrimidin (fenclorim), 1-(2,4-dichlor-phenyl)-5-trichloromethyl-1H-1,2,4-triazol-3-carboxylsyre-ethylester (fenchlorazol-ethyl), 2-chlor-4-trifluormethyl-thiazol-5-carboxylsyre-phenylmethylester (flurazoler), 4-chlor-N-(1,3-dioxolan-2-yl-methoxy)-α-trifluor-acetophenonoxim (fluxofenim), 3-dichloracetyl-5-(2-furanyl)-2,2-dimethyloxazolidin (furilazoler, MON-13900), ethyl-4,5-dihydro-5,5-diphenyl-3-isoxazolcarboxylat (isoxadifen-ethyl), diethyl-1-(2,4-dichlorphenyl)-4,5-dihydro-5-methyl-1H-pyrazol-3,5-dicarboxylat (mefenpyr-diethyl), 2-dichlormethyl-2-methyl-1,3-dioxolan (MG-191), 1,8-naphthalsyreanhydrid, α-(1,3-dioxolan-2-yl-methoximino)-phenylacetonitril (oxabetrinil), 2,2-dichlor-N-(1,3-dioxolan-2-yl-methyl)-N-(2-propenyl)-acetamid
(PPG-1292), 3-dichloracetyl-2,2-dimethyl oxazolidin (R-28725),
3-dichloracetyl-2,2,5-trimethyl-oxazolidin (R-29148), 1-(2-
chlor-phenyl)-5-phenyl-1H-pyrazol-3-carboxyksyre-methylester
og N-(2-methoxy-benzoyl)-4-[(methylamino-carbonyl)-amino]-
benzensulfonamid
("aktivstoffer fra gruppe 3").

2. Middel ifølge krav 1, kendetegnet ved, at de forbindelser,
der forbedrer kulturplanteforlørligheden (bestanddel (c)), er
udvalgt af de følgende nævnte aktivstoffer:
5-chlor-quinolin-8-oxy-eddikesyre-(1-methyl-hexylester)
(cloquintocet-mexyl) og diethyl-1-(2,4-dichlor-phenyl)-4,5-
dihydro-5-methyl-1H-pyrazol-3,5-dicarboxylat (mefenpyr-
diethyl).

3. Middel ifølge et af kravene 1 og 2, kendetegnet ved, at der
til en vægtdel aktivstof fra gruppe 1 bruges 0,01 til 1.000
vægtdele af aktivstoffet eller af aktivstofferne fra den anden
gruppe af herbicider (bestanddel (b)).

4. Middel ifølge et af kravene 1 til 3, kendetegnet ved, at
der til en vægtdel aktivstof fra gruppe 1 eller blandinger
heraf med aktivstoffer fra den anden gruppe af herbicider
(bestanddel (b)) bruges 0,001 til 1.000 vægtdele af det
aktivstof, der forbedrer kulturplanteforlørligheden, eller de
aktivstoffer, der forbedrer kulturplanteforlørligheden
(bestanddel (c)).

5. Anvendelse af et middel ifølge et af kravene 1 til 4 til
bekæmpelse af uønskede planter.

6. Fremgangsmåde til bekæmpelse af uønskede planter,
kendetegnet ved, at man lader midler ifølge et af kravene 1
til 4 indvirke på de uønskede planter og/eller deres levested.

7. Fremgangsmåde til fremstilling af et herbicidt middel,
kendetegnet ved, at man blander et middel ifølge et af kravene
1 til 4 med overfladeaktive midler og/eller strækmidler.