



(86) Date de dépôt PCT/PCT Filing Date: 2001/04/04
 (87) Date publication PCT/PCT Publication Date: 2001/10/11
 (85) Entrée phase nationale/National Entry: 2002/09/30
 (86) N° demande PCT/PCT Application No.: EP 2001/003833
 (87) N° publication PCT/PCT Publication No.: 2001/074157
 (30) Priorités/Priorities: 2000/04/04 (60/194,383) US;
 2000/09/11 (60/231,631) US

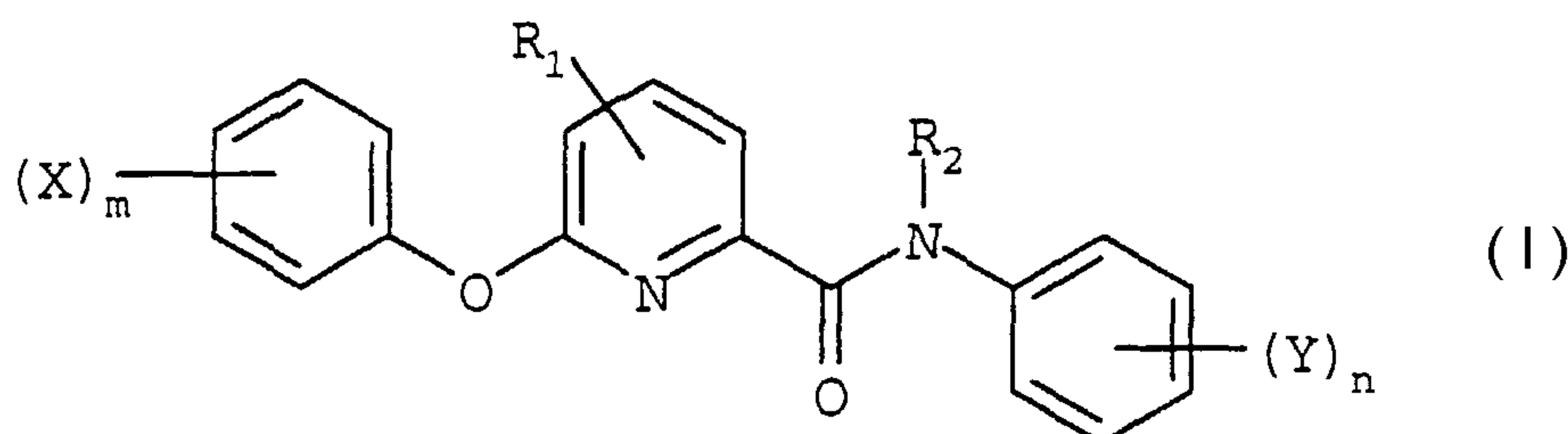
(51) Cl.Int.⁷/Int.Cl.⁷ A01N 43/40, A01N 43/82, A01N 43/653,
 A01N 37/46

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(54) Titre : MELANGES HERBICIDES SYNERGIQUES
 (54) Title: SYNERGISTIC HERBICIDAL MIXTURES



(57) **Abrégé/Abstract:**

The present invention provides cereal selective herbicidal compositions comprising a herbicidally acceptable carrier and/or surfactant and, as active ingredient, herbicidally effective amount of at least one 6-phenoxy-pyridin-2-yl-carboxamide of formula (I) and at least one additional herbicidal compound selected from the group consisting of flufenacet, cinidon-ethyl and carfentrazone-ethyl. Also provided is a method for the control of undesirable plants such as *Setaria viridis*, *Alopecurus myosuroides*, *Poa annua*, *Stellaria media*, *Lamium purpureum*, *Galium aparine*, *Veronica hederaefolia*, *Papaver rhoeas* and *Matricaria inodora* which comprises applying to the plants of their locus a herbicidally effective amount of said compositions. The compositions have been found to possess synergistic properties.

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

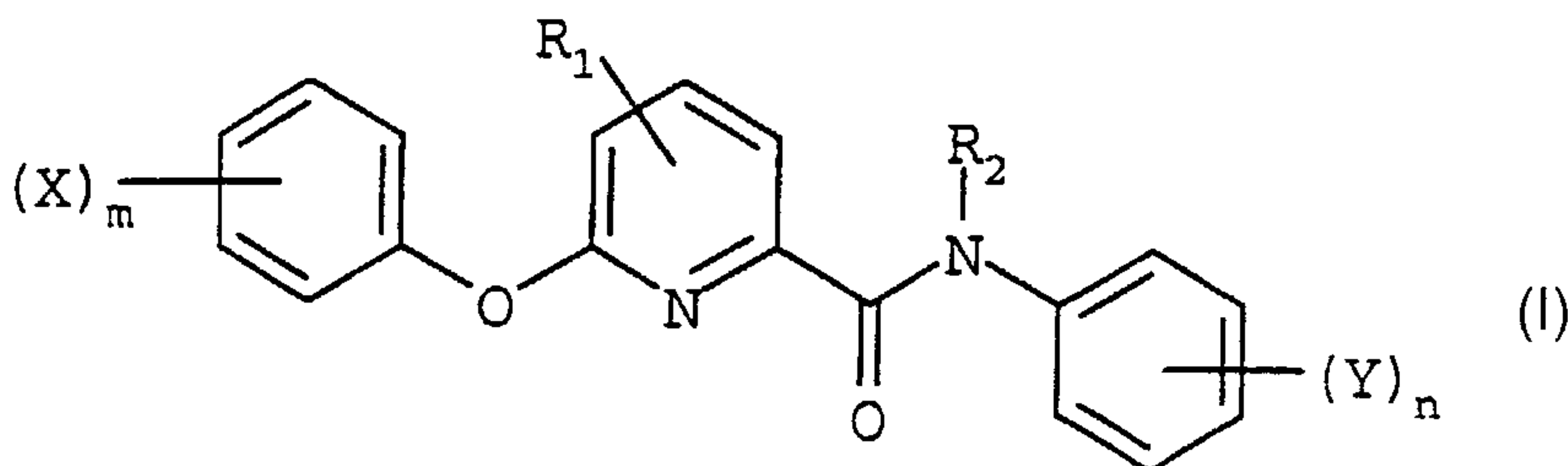
(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
11 October 2001 (11.10.2001)

PCT

(10) International Publication Number
WO 01/074157 A3

- (51) International Patent Classification⁷: A01N 43/40 // (A01N 43/40, 43:82, 43:653, 37:46)
- (21) International Application Number: PCT/EP01/03833
- (22) International Filing Date: 4 April 2001 (04.04.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/194,383 4 April 2000 (04.04.2000) US
60/231,631 11 September 2000 (11.09.2000) US
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EE, 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, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
- (88) Date of publication of the international search report:
18 July 2002
- 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: SYNERGISTIC HERBICIDAL MIXTURES



(57) Abstract: The present invention provides cereal selective herbicidal compositions comprising a herbicidally acceptable carrier and/or surfactant and, as active ingredient, herbicidally effective amount of at least one 6-phenoxy-pyrid-2-ylcarboxamide of formula (I) and at least one additional herbicidal compound selected from the group consisting of flufenacet, cinidon-ethyl and carfentrazone-ethyl.

Also provided is a method for the control of undesirable plants such as *Setaria viridis*, *Alopecurus myosuroides*, *Poa annua*, *Stellaria media*, *Lamium purpureum*, *Galium aparine*, *Veronica hederifolia*, *Papaver rhoeas* and *Matricaria inodora* which comprises applying to the plants of their locus a herbicidally effective amount of said compositions. The compositions have been found to possess synergistic properties.

WO 01/074157 A3

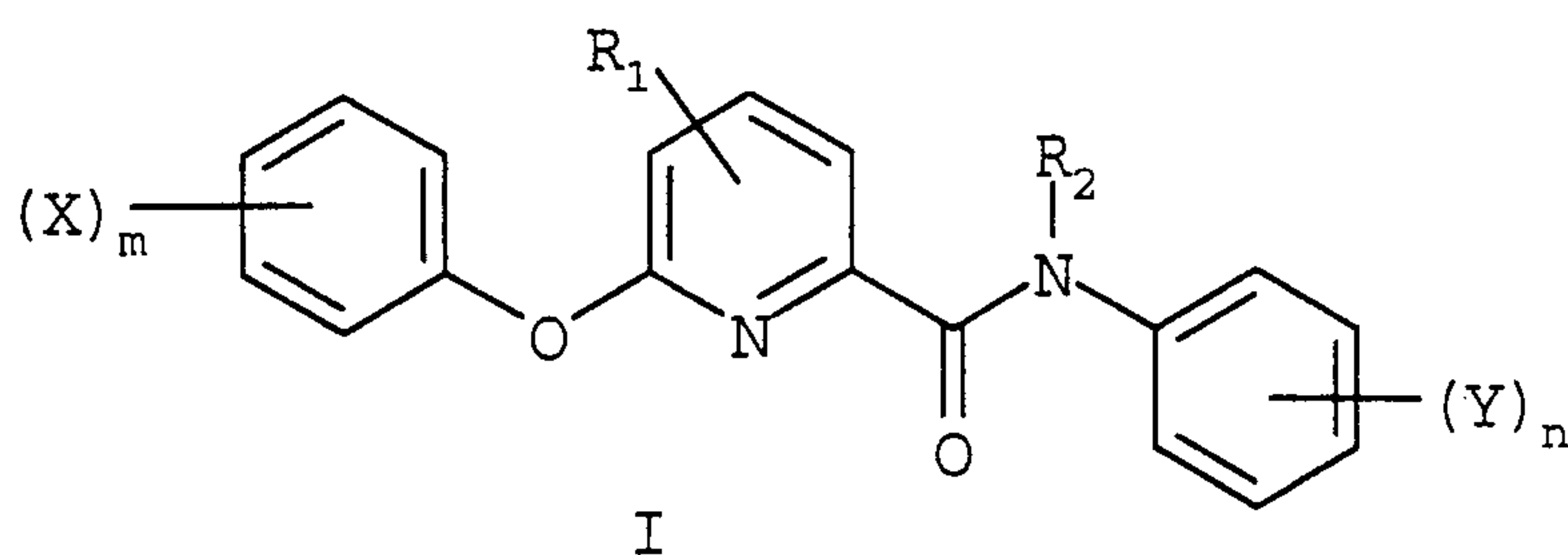
SYNERGISTIC HERBICIDAL MIXTURES

Herbicide 6-phenoxy-pyrid-2-ylcarboxamides such as those disclosed U.S. Patent 5,294,597 display excellent herbicidal performance, in particular against broad-leaved weeds in crops such as cereal crops. However, when used as the sole active ingredient, the 6-phenoxy-pyrid-2-ylcarboxamides do not always achieve effective control of the full spectrum of weed species encountered in commercial agronomic applications, in conjunction with reliable selectivity for the crop species. Such gaps in the spectrum of control can be overcome by co-treatment with another herbicide known to be effective against the relevant weed species. The combined use of these 6-phenoxy-pyrid-2-ylcarboxamides with special further and other herbicides has been described in U.S. Patent 5,674,807.

Therefore it is an object of this invention to provide further herbicide combinations which exhibit a good herbicidal action exceeding the activity of one active ingredient alone, in particular in cereal crops.

It is another object of this invention to provide methods for controlling undesired vegetation, in particular dicotyledonous weeds, using the herbicide combinations. It is a further object of this invention to provide the method of use of the herbicide combinations for controlling undesired vegetation, in particular in cereal crops, and in particular against dicotyledonous weeds.

We have found that this object is achieved by herbicide compositions which comprise an agriculturally acceptable carrier and a herbicidally effective amount of a combination of at least one 6-phenoxy-pyrid-2-ylcarboxamide of formula I



wherein

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- R₁ represents a hydrogen or halogen atom or an alkyl or alkoxy group;
- R₂ represents a hydrogen atom or an alkyl group;
- 5 X each independently represents a halogen atom or an optionally substituted alkyl or alkoxy group or an alkenyloxy, cyano, carboxy, alkoxycarbonyl, (alkylthio)carbonyl, alkylcarbonyl, amido, alkylamido, dialkylamido, nitro, alkylthio, haloalkyl-
- 10 thio, alkenylthio, alkynylthio, alkylsulphanyl, alkylsulphonyl, alkyloximinoalkyl or alkenyloximinoalkyl group;
- m represents 0 or an integer from 1 to 5;
- 15 Y each independently represents a halogen atom or an alkyl, nitro, cyano, haloalkyl, alkoxy or haloalkoxy group;
- n represents 0 or an integer from 1 to 5, and
- 20 at least one additional herbicidal compound selected from the group consisting of flufenacet, cinidon-ethyl and carfentrazone-ethyl.

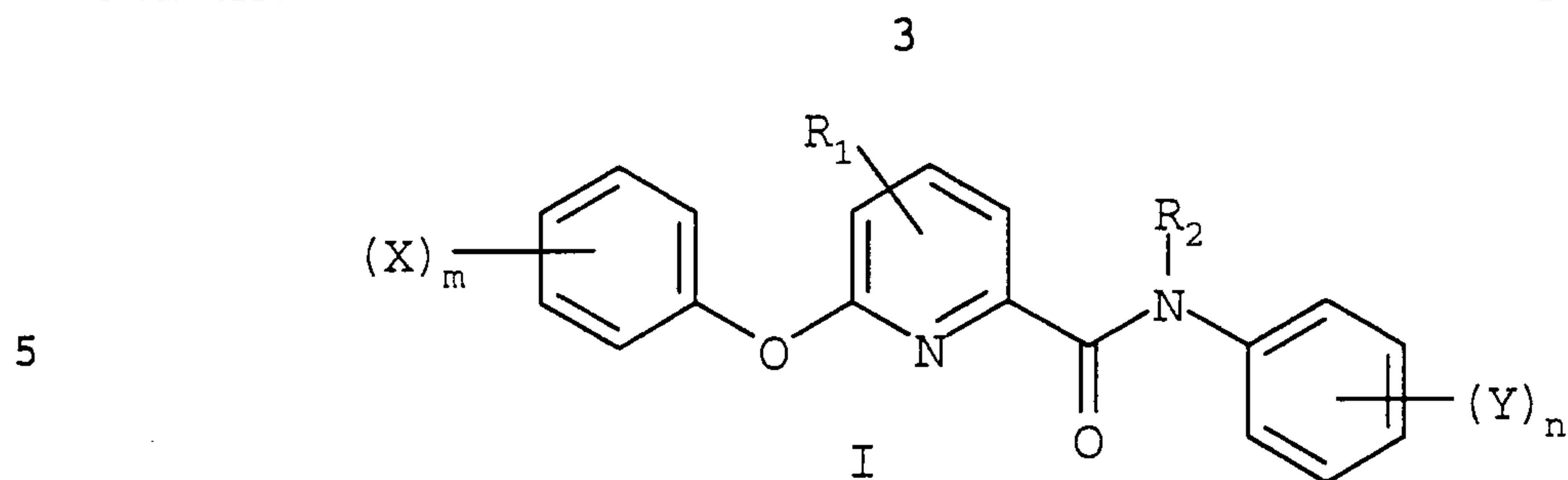
The present invention also provides a method for controlling
25 undesirable plant species comprising application of said compositions. In the method of this invention, these compounds may be applied separately or together, in herbicidally effective amounts, and in the presence of a crop, preferably a cereal crop, such as wheat.

30 Although 6-phenoxy-pyrid-2-ylcarboxamides such as those disclosed in U.S. Patent 5,294,597 display excellent herbicidal performance, when used as the sole active ingredient, they do not always achieve effective control of the full spectrum of weed
35 species encountered in commercial agronomic applications, in conjunction with reliable selectivity for the crop species.

It has now been found that combinations comprising a 6-phenoxy-pyrid-2-ylcarboxamide of formula I

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10 wherein R_1 , R_2 , X , Y , m and n are defined as above,

with at least one additional herbicidal compound selected from the group of flufenacet, cinidon-ethyl or carfentrazone-ethyl provide synergistic control of troublesome broad-leaved weeds and
 15 annual grasses, especially such as *Setaria viridis*, *Alopecurus myosuroides*, *Poa annua*, *Stellaria media*, *Lamium purpureum*, *Galium aparine*, *Veronica hederaefolia*, *Papaver rhoeas* and *Matricaria inodora*. That is, application of the combination of the invention gives a mutual reinforcing action such that the application rates
 20 of the individual herbicidal component can be reduced and still the same herbicidal effect is achieved or, alternatively, the application of the combination of herbicidal components demonstrates a greater herbicidal effect than expected from the effect of the application of the individual herbicidal components when
 25 applied singly at the rate at which they are present in the combination (synergistic effect).

In the specification and claims, alkyl groups, unless otherwise specified, may be linear or branched and may contain up to 12,
 30 preferably 1 to 4, carbon atoms. The alkenyl or alkynyl portion of an alkynyloxy, alkenylthio or alkynylthio group, unless otherwise specified, may be linear or branched and may contain up to 12, preferably 2 to 4, carbon atoms. Examples of such groups are methyl, ethyl, propyl, vinyl, allyl, isopropyl, butyl, isobutyl
 35 and tertiary-butyl groups. The alkyl portion of a haloalkyl, haloalkoxy, alkylthio, haloalkylthio, alkoxy, alkoxy carbonyl, (alkylthio)carbonyl, alkylamido, dialkylamido, alkylsulfinyl or alkylsulfonyl group suitably has from 1 to 4 carbon atoms, preferably 1 or 2 carbon atoms. The number of carbon atoms in the
 40 alkyloximinoalkyl or alkenyloximinoalkyl groups is up to 6, preferably up to 4, e.g. 2-methoximinoethyl, 2-methoximinopropyl or 2-ethoximinopropyl.

"Halogen" means a fluorine, chlorine, bromine or iodine atom,
 45 preferably fluorine, chlorine or bromine. Haloalkyl, haloalkylthio and haloalkoxy are preferably mono-, di- or trifluoroalkyl,

-alkylthio and -alkoxy, especially trifluoromethyl, difluoromethoxy, trifluoromethylthio and trifluoromethoxy.

When any groups are designated as being optionally substituted, 5 the substituent groups which are optionally present may be any of those customarily employed in the modification and/or development of pesticidal compounds and are especially substituents that maintain or enhance the herbicidal activity associated with the compounds of the present invention, or influence persistence of 10 action, soil or plant penetration, or any other desirable property of such herbicidal compounds. There may be one or more of the same or different substituents present in each part of the molecules. In relation to moieties defined above as comprising optionally substituted alkyl- and alkoxy groups, specific 15 examples of such substituents include phenyl, halogen atoms, nitro, cyano, hydroxyl, C₁₋₄-alkoxy, C₁₋₄-haloalkoxy and C₁₋₄-alkoxycarbonyl groups.

A preferred embodiment of the invention provides herbicidal com- 20 positions which comprise an agriculturally acceptable carrier and a herbicidally effective amount of a combination of at least are 6-phenoxy pyrid-2-ylcarboxamide of formula I and at least flufenacet as additional herbicidal compound.

25 A further preferred embodiment of the invention provides herbicidal compositions which comprise an agriculturally acceptable carrier and a herbicidally effective amount of a combination of at least one 6-phenoxy pyrid-2-ylcarboxamide of formula I and at least carfentrazone-ethyl as additional herbicidal compound.

30 A further preferred embodiment of the invention provides herbicidal compositions which comprise an agriculturally acceptable carrier and a herbicidally effective amount of a combination of at least one 6-phenoxy pyrid-2-ylcarboxamide of formula I and at 35 least cinidon-ethyl.

Preferred compounds for use as 6-phenoxy pyrid-2-ylcarboxamides according to the invention are compounds of formula I, wherein

40 R₁ represents a hydrogen atom or a C₁₋₄-alkoxy group;

R₂ represents a hydrogen atom;

X represents a halogen atom or a C₁₋₄-haloalkyl group;

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m represents an integer from 1 to 3, in particular 1;

Y represents preferably a halogen atom or a C₁₋₄-haloalkyl group;
and

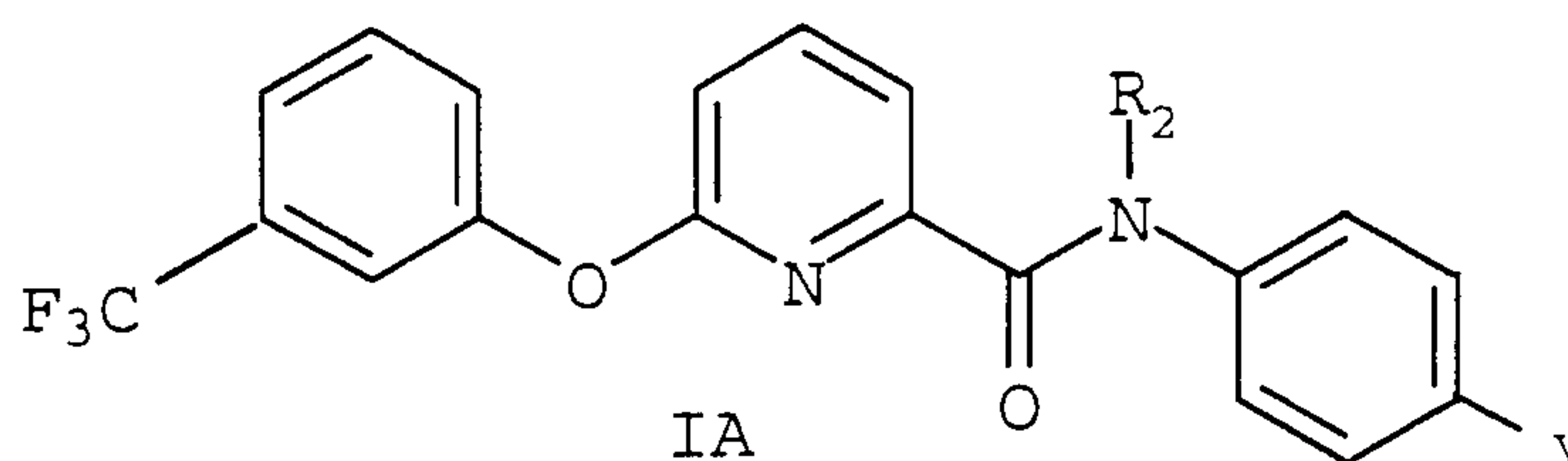
n represents an integer from 1 to 3, in particular 1.

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Especially preferred compounds for use as 6-phenoxy-pyrid-2-ylcarboxamides according to the invention are the compounds of formula IA,

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in particular N-(4-fluorophenyl)-6-(-3-trifluoromethyl-
20 phenoxy)-pyrid-2-ylcarboxamide coded picolinafen.

A preferred embodiment of the present invention provides a herbicidal composition which comprises an agriculturally acceptable carrier and a herbicidally effective amount of a combination of
25 picolinafen and flufenacet.

A further preferred embodiment of the present invention provides a herbicidal composition which comprises an agriculturally acceptable carrier and a herbicidally effective amount of a combination of
30 picolinafen and cinidon-ethyl.

A further preferred embodiment of the present invention provides a herbicidal composition which comprises an agriculturally acceptable carrier and a herbicidally effective amount of a combination of
35 picolinafen and carfentrazone-ethyl.

Flufenacet is the proposed common name of N-(4-fluorophenyl)-N-(1-methylethyl)-2-([5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy)acetamide, which is disclosed for example in U.S. Patent
40 5,090,991.

Cinidon-ethyl is the common name of ethyl (Z)-2-chloro-3-[2-chloro-5-(1,3-dioxo-4,5,6,7-tetrahydroisindol-2-yl)-phenyl]-acrylate, which is disclosed for example by K. Grossmann, H.
45 Schiffer, Pestic. Sci. (1999), 55(7), 687-695. CODEN: PSSCBG
ISSN: 0031-613X.

Carfentrazone-ethyl is the common name of ethyl (RS)-2-chloro-3-[2-chloro-5-(4-difluoromethyl-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl)-4-fluorophenyl]propionate, which is reported by W. A. Van Saun et al, Proc Br. Crop. Prot. Conf., Weeds, 1993, 5 1, 19.

The pattern of persistence of the compounds of formula I is such that the combined treatment according to the present invention can be attained either by the application of a prepared mixture 10 as defined above, or by time separated application of separate formulations. Hence, in another preferred embodiment, the present invention provides a method for controlling the growth of weeds at a crop locus which comprises applying to the locus a compound of formula I as defined above and a second component selected 15 from the group consisting of flufenacet, cinidon-ethyl and carfentrazone-ethyl and mixtures thereof.

The treatment according to the invention may be used to control a broad spectrum of weed species in crops, particularly cereal 20 crops such as in wheat, barley, rice and maize, by pre- or post-emergence treatment, including both early and late post-emergence. The combined use described above offers both foliar and residual activity.

25 By the term "pre-emergence application" is meant application to the soil in which the weed seeds or seedlings are present before emergence of the weeds above the surface of the soil. By the term "post-emergence application" is meant application to the aerial or exposed portions of the weeds which have emerged above the 30 surface of the soil. It will be appreciated that application according to the method may be from pre- to post-weed emergence, and from pre-crop emergence to post-crop emergence. If one of the active ingredients or the composition of the active ingredients is less well tolerated by certain crop plants, application tech- 35 niques may be employed in which the herbicidal composition is sprayed, with the aid of the spraying equipment, in such a way that the leaves of the sensitive crop plants come into as little contact as possible, if any, with ten active ingredient(s), while the latter reach the leaves of undesired plants which grow un- 40 derneath, or the naked surface (post directed, lay-by). By the term "foliar activity" is meant herbicidal activity obtained by application to the aerial or exposed portions of the weeds which have emerged above the surface of the soil. By the term "residual activity" is meant herbicidal activity obtained some time after 45 application to the soil whereby seedlings present at the time of

application or which germinate subsequent to application are controlled.

Weeds that may be controlled by the practice of the present invention include:

	<i>Agrostis stolonifera</i>	<i>Lolium perenne</i>
	<i>Alopecurus myosuroides</i>	<i>Matricaria inodora</i>
	<i>Anthemis arvensis</i>	<i>Matricaria matricoides</i>
10	<i>Apera spica-venti</i>	<i>Montia perfoliata</i>
	<i>Aphanes arvensis</i>	<i>Myosotis arvensis</i>
	<i>Arenaria seryllifolia</i>	<i>Papaver rhoeas</i>
	<i>Atriplex patula</i>	<i>Phalaris minor</i>
	<i>Avena fatua</i>	<i>Phalaris paradoxa</i>
	<i>Bromus sterilis</i>	<i>Poa annua</i>
15	<i>Capsella bursa-pastoris</i>	<i>Poa trivialis</i>
	<i>Centaurea cyanus</i>	<i>Polygonum aviculare</i>
	<i>Cerastes holosteoides</i>	<i>Polygonum convolvulus</i>
	<i>Chenopodium album</i>	<i>Polygonum lapathifolium</i>
	<i>Chrysanthemum segetum</i>	<i>Portulaca oleracea</i>
20	<i>Cirsium arvense</i>	<i>Raphanus raphanistrum</i>
	<i>Eleusine indica</i>	<i>Senecia vulgaris</i>
	<i>Euphorbia helioscopia</i>	<i>Setaria viridis</i>
	<i>Fumaria officinalis</i>	<i>Silene vulgaris</i>
	<i>Galeopsis tetrahit</i>	<i>Spergula arvensis</i>
	<i>Galium aparine</i>	<i>Stellaria media</i>
25	<i>Geranium dissectum</i>	<i>Thlaspi arvense</i>
	<i>Lamium amplexicaule</i>	<i>Veronica hederaefolia</i>
	<i>Lamium purpureum</i>	<i>Veronica persica</i>
	<i>Legousia hybrida</i>	<i>Viola arvensis</i>

30 The necessary application rate of active ingredient composition without formulation auxiliaries, depends on the composition of the plant stand, on the development stage of the plants, on the climatic conditions at the site of action, and on the application technique. In general, the application rate of the active inge-

35 dients together is from 0.001 to 10 kg a.I./ha; preferably from 0.001 to 3 kg ha, in particular 0.01 to 1 kg/ha. In another embodiment of the invention the application rate of the active ingredients together is from 0.01 to 10 kg a.i./ha.

40 The application rate of the compound of formula I is usually in the range of 5 to 500, preferably 7.5-200 grams of active ingredient (g a.i.) per hectare, with rates between 10-100 g a.i./ha often achieving satisfactory control and selectivity. The optimal rate for a specific application will depend on the

45 crop(s) under cultivation and the predominant species of infest-

ing weed, and readily may be determined by established biological tests known to those skilled in the art.

The selection of the herbicidally active second component will likewise be dependent on the crop/weed situation to be treated, and will be readily identifiable by those skilled in this area. The application rate for this second component is determined primarily by the chemical type of the component, since the intrinsic activity of different types of herbicide varies widely. In general, the preferred application rate for flufenacet is in the range of 7.5-400, preferably 10-200 g a.i./ha; the preferred application rate for cinidon-ethyl is in the range of 10-500, preferably 15-250 g/ha; the preferred application rate for carfentrazone-ethyl is in the range of 1-150, preferably 2.5-75 g/ha. The optimal rate for the second component will, however, depend on the crop(s) under cultivation and the level of weed infestation, and can readily be determined by established biological tests. Naturally, with such a wide variation in application rate for the second component, the ratio of a formula I compound to a second component in the present invention will be determined predominantly by the choice of the second component. In general the compound of formula I and the second herbicide are employed in such weight ratios that the synergistic effect is observed. The ratio (by weight) of compound of formula I to the second herbicidal compound is as a rule, from 1000:1 to 1:100, preferably from 100:1 to 1:20, in particular from 10:1 to 1:10.

In a preferred embodiment. The ratio (by weight) of compound of formula I to the second herbicidal compound is as a rule, from 100:1 to 1:100, preferably from 20:1 to 1:20, in particular from 10:1 to 1:10. The preferred formula I to second component ratio may vary, e.g., from about 5 : 1 to about 1 : 5.

In another preferred embodiment the ratio (by weight) of compound of formula I to the second herbicidal compound is as a rule from 1000:1 to 1:10, preferably from 100:1 to 1:5, in particular from 10:1 to 1:3,3.

Preferably the compound of formula I is picolinafen and the second compound is cinidon-ethyl.

The active compounds can be used in the form of a mixture of separate formulations, typically mixed with water prior to application (tank-mixtures), or as separate formulations applied individually within a certain time interval. Both active compounds can also be formulated together in a suitable ratio ac-

ording to the present invention, together with usual carriers and/or additives known in the art.

Accordingly, the invention further provides a herbicidal composition which comprises as active ingredient, a herbicidally effective amount of at least one compound of formula I as defined above, and at least one compound selected from group consisting of flufenacet, cinidon-ethyl, carfentrazone-ethyl and one or more carriers. Another embodiment of the invention provides a herbicidal composition which comprises as active ingredient a herbicidally affective amount of at least one compound of formula I as defined above, and at least one compound selected from the group consisting of flufenacet, cinidon-ethyl and carfentrazone-ethyl, one or more carriers and at least one surfactant. A method of making such a composition is also provided which comprises bringing the mixture of the compound of formula I and the second component into association with the carrier(s) and if desired with the surfactant(s).

A composition according to the invention generally comprise approximately from 0.001% to 98% by weight (w/w) of active ingredients, preferably contains from 0.01% to 95% by weight (w/w), in particular from 0.5% to 95% by weight (w/w) . The active ingredients are employed in a purity of 80% to 100%, preferably 90% to 100%, in particular 95% to 100% (according to NMR-Spectrum).

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage, transport or handling. A carrier may be a solid or a liquid, including material which is normally a gas but which has been compressed to form a liquid.

The compositions may be manufactured into e.g. emulsion concentrates, solutions, oil in water emulsions, wettable powders, soluble powders, suspension concentrates, dusts, granules, water dispersible granules, micro-capsules, gels and other formulation types by well-established procedures. These procedures include intensive mixing and/or milling of the active ingredients with other substances, such as fillers, solvents (liquid carriers), solid carriers, surface active compounds (surfactants), and optionally solid and/or liquid auxiliaries and/or adjuvants such as wetters, adhesives, dispersants or emulsifiers.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients(s) and if desired other substances, such as surface active compounds, liquid auxiliaries and/or adjuvants, to the
5 solid carrier.

Suitable liquid carriers (solvents) are essentially: mineral oil fractions of medium to high boiling point such as kerosine and diesel oil, furthermore coal tar oils and oils of vegetable or
10 animal origin; aliphatic, cyclic and aromatic hydrocarbons, for example cyclohexane, parafins, tetrahydronaphthalene, alkylated naphthalenes and their derivatives, alkylated benzenes and their derivatives (such as Solvesso® 200); phthalic acid esters, such as dibutyl or dioctyl phthalate; alcohols and glycols as well as
15 their ethers and esters, e.g. methanol, ethanol, propanol, butanol, cyclohexanol, ethylene glycol mono- and dimethyl ether; ketones such as cyclohexenone; strongly polar solvents, for examples amines such as N-methyl pyrrolidone, N-octylpyrrolidone and N-cyclohexylpyrrolidone, or lactones such as γ -butyrolactone;
20 epoxidized plant oil esters such as methylated coconut or soybean oil ester; and water. Mixtures of different liquid carriers are often suitable.

Surfactants may be nonionic, anionic, cationic or zwitterionic
25 substances with good dispersing, emulsifying and wetting properties depending on the nature of the compound according to general formula I and/or the additional herbicidal compound selected from the group consisting flufenacet, cinidon-ethyl and carfentrazone-ethyl to be formulated. Surfactants may also mean
30 mixtures of individual surfactants.

Solid carriers are essentially:

mineral earth such as silicas, silica gels, silicates, talc, kaolin,
35 lin, montmorillonite, attapulgit, pumice, sepiolite, bentonite, limestone, lime, chalk, bole, loes, clay, dolomite, diatomaceous earth, calcite, calcium sulfate, magnesium sulfate, magnesium sulfate, magnesium oxide, sand, ground plastics, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas,
40 and crushed products of vegetable origin such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders, or other solid carriers.

Suitable surfactants are the alkali metal salts, alkaline earth
45 metal salts and ammonium salts of aromatic sulfonic acids, for example lignin-, phenol-, naphthalene- and dibutyl-naphthalene-sulfonic acid, and of fatty acids, of alkyl- and alkylaryl-sulfo-

nates, of alkyl, lauryl ether and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols and of fatty alcohol glycol ether, and condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenyl and tributylphenyl polyglycol ethers, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignin-sulfite waste liquors or methylcellulose.

Pesticidal compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a surfactant facilitate this process of dilution. Thus, preferably a composition according to the invention comprises if desired at least one surfactant. For example, the composition may contain one or more carriers and at least one surfactant.

The compositions of the invention may for example be formulated as wettable powders, water dispersible granules, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 5 to 90% w/w of active ingredient and usually contain in addition to solid inert carrier, 3 to 10% w/w of dispersing and wetting agents and, where necessary, 0 to 10% w/w of stabilizer(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and may be diluted in the field with further solid carrier to give a composition usually containing 0.5 to 10% w/w of active ingredient. Water dispersible granules and granules are usually prepared to have a size between 0.15 mm and 2.0 mm and may be manufactured by a variety of techniques. Generally, these types of granules will contain 0.5 to 90% w/w active ingredient and 0 to 20% w/w of additives such as stabilizer, surfactants, slow release modifiers and binding agents. The so-called "dry flowables" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent or a mixture of solvents, 1 to 80% w/v active ingredient, 2 to 20% w/v emulsifiers and 0 to 20% w/v of other additives such as stabilizers, penetrants and corrosion inhibitors. Suspension concentrates are usually milled so as to obtain a stable, non-sedimenting flowable product and usually contain 5 to 75% w/v active ingredient, 0.5 to 15% w/v of dis-

- persing agents, 0.1 to 10% w/v of suspending agents such as protective colloids and thixotropic agents, 0 to 10% w/v of other additives such as defoamers, corrosion inhibitors, stabilizers, penetrants and retention enhancers (stickers), and water or an
5 organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation and crystallization or as antifreeze agents for water.
- 10 The forms of application of the compositions according to the invention depend on the intended purposes; in any case, they should guarantee as fine as possible a distribution of the active ingredients. They can be applied, for example, in the form of directly sprayable aqueous solutions, powders, suspensions, also
15 highly-concentrated aqueous, oily or other suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for spreading or granules, by spraying, atomizing, dusting or pouring.
- 20 Aqueous use forms can be prepared from emulsion concentrates, suspensions, pastes, wettable powders or water-dispersible granules by adding water. To prepare emulsions, pastes or oil dispersions, the herbicidally active ingredients as such or dissolved in an oil or solvent, can be homogenized in water by
25 means of wetters, adhesives, dispersants or emulsifiers.

Alternatively, concentrates which consist of herbicidally active ingredients, wetter, adhesive, dispersant or emulsifier and, if appropriate solvent or oil may be prepared, and such concentrates
30 are suitable for dilution with water.

Aqueous dispersions and emulsions, for example compositions obtained by diluting the formulated product according to the invention with water, also lie within the scope of the invention.

35 Of particular interest in enhancing the duration of the protective activity of the compounds of this invention is the use of a carrier which will provide slow release of the pesticidal compounds into the environment of a plant which is to be pro-
40 tected.

The biological activity of the active ingredient can also be increased by including an adjuvant in the spray dilution. An adjuvant is defined here as a substance which can increase the
45 biological activity of an active ingredient but is not itself significantly biologically active. The adjuvant can either be included in the formulation as a coformulant or carrier, or can be

added to the spray tank together with the formulation containing the active ingredient.

As a commodity the compositions may preferably be in a concentrated form whereas the end user generally employs diluted compositions. The compositions may be diluted to a concentration down to 0.001% of active ingredient, usually the formulation comprise approximately from 0.001 to 98% by weight, preferably 0.01 to 95% by weight, of active ingredients. The doses usually are in the range from 0.01 to 10 kg a.i./ha.

Examples of formulations according to the invention are:

Emulsion Concentrate (EC)

15

Active Ingredient	Picolinafen + flufenacet (1 : 2)	30 % (w/v)
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20

Emulsifier(s)	Atlox [®] 4856 B / Atlox [®] 4858 B 1) (mixture containing calcium alkyl aryl sulfonate, fatty alcohol ethoxylates and light aromatics)	5 % (w/v)
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25

Solvent	Shellsol [®] A 2) (mixture of C ₉ - C ₁₀ aromatic hydrocarbons)	to 1000 ml
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Suspension Concentrate (SC)

30

Active Ingredient	Picolinafen + carfentrazone-ethyl (4 : 1)	50 % (w/v)
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35

Dispersing agent	Soprophor [®] FL 3) (polyoxyethylene polyaryl phenyl ether phosphate amine salt)	3 % (w/v)
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40

Antifoaming agent	Rhodorsil [®] 422 3) (nonionic aqueous emulsion of polydimethylsiloxanes)	0.2 % (w/v)
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45

Structure agent	Kelzan [®] S 4) (Xanthan gum)	0.2 % (w/v)
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	Antifreezing agent	Propylene glycol	5 % (w/v)
5	Biocidal agent	Proxel [®] 5) (aqueous dipropylene glycol solution containing 20% 1,2-beniso-thiazolin-3-one)	0.1 % (w/v)
10	Water		to 1000 ml
	Wettable Powder (WP)		
15	Active Ingredient	Picolinafen + flufenacet (1 : 2)	60 % (w/w)
	Wetting agent	Atlox [®] 4995 1) (polyoxyethylene alkyl ether)	2 % (w/w)
20	Dispersing agent	Witcosperse [®] D-60 6) (mixture of sodium salts of condensed naphthalene sulfonic acid and alkylaryl polyoxy acetates)	3 % (w/w)
25	Carrier / Filler	Kaolin	35 % (w/w)
	Water Dispersible Granules (WG)		
30	Active Ingredient	Picolinafen + carfentrazone-ethyl (4 : 1)	50 % (w/w)
35	Dispersing / Binding agent	Witcosperse [®] D-450 6) (mixture of sodium salts of condensed naphthalene sulfonic acid and alkyl sulfonates)	8 % (w/w)
40	Wetting agent	Morwet [®] EFW 6) (formaldehyde condensation product)	2 % (w/w)
45	Antifoaming agent	Rhodorsil [®] EP 6703 3) (encapsulated silicone)	1 % (w/w)

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15

Disintegrant Agrimer® ATF 7) 2 % (w/w)
(cross-linked homopolymer of N-vinyl-2-pyrrolidone)

5 Carrier / Kaolin 35 % (w/w)
Filler

- 1) commercially available from ICI Surfactants
- 10 2) commercially available from Deutsche Shell AG
- 3) commercially available from Rhône-Poulenc
- 4) commercially available from Kelco Co.
- 5) commercially available from Zeneca
- 6) commercially available from Witco
- 15 7) commercially available from International Speciality Products

The compositions of this invention can also comprise other compounds having biological activity, e.g. compounds having similar or complementary pesticidal activity or compounds having
20 plant growth regulating, fungicidal, or insecticidal or antibacterial activity. These mixtures of pesticides can have a broader spectrum of activity than the synergistic composition according to this invention alone. Also of interest is the mixability with
25 mineral salt solutions, which are employed for treating nutritional and trace element deficiencies. Nonphytotoxic oils and oil concentrates may also be added.

The following examples illustrate specific embodiments of the present invention; however, the invention is not limited to the
30 embodiments so illustrated, but includes the entire scope of the appended claims.

For a more clear understanding of the invention, specific examples thereof are set forth below. These examples are merely
35 illustrative, and are not to be understood as limiting the scope and underlying principles of the invention in any way.

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In the following examples, synergism for two-way combinations is determined by the Colby¹ method, i.e. the expected (or predicted) response of the combination is calculated by taking the product of the observed response for each individual component of the combination when applied alone divided by 100 and subtracting this value from the sum of the observed response for each component when applied alone. Synergism of the combination is then determined by comparing the observed response of the combination to the expected (or predicted) response as calculated from the observed responses of each individual component alone. If the observed response of the combination is greater than the expected (or predicted) response then the combination is said to be synergistic and falls within the definition of synergistic effect as previously defined.

15

The foregoing is illustrated mathematically below, wherein a two-way combination, C₂, is composed of component X plus component Y and Obs. designates the observed response of the combination C₂.

20 Postemergence Herbicidal Greenhouse Evaluations

Test Serie A

Plant seeds are sown in pots containing a loamy sand soil (0.5 l). The herbicides are applied as single treatments, or in a combination comprising a compound of formula I and a second compound as defined above, after emergence of weeds and crop. The herbicidal performance is assessed as percent damage in comparison to the untreated control plants. The assessment is done 21 days after the treatment. Wheat and barley are treated at the 3-4 leaf stage, the broad-leaf weeds at the 2-4 leaf stage and annual grasses at the 2-3 leaf stage.

35

¹ Colby, S. R., Weeds, 1967(15), p. 20-22

40

XY

$$(X + Y) - \frac{XY}{100} = \text{Expected response (Exp.)}$$

100

45

$$\text{Synergism} \equiv \text{Obs.} > \text{Exp.}$$

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For the compound of formula I picolinafen is employed. The second component has application rates (and hence component ratios) chosen to be appropriate to the established activity level of that component.

5

The following abbreviations have been used in the tables:

EXP is the expected response by means of the Colby formula.

10 OBS is the observed response.

The damage caused by the chemicals was assessed with reference to a scale from 0 to 100% in comparison with the untreated control plants. 0 means no damage and 100 means complete destruction of
15 the plants.

Table I gives the results of the postemergence herbicidal activity of picolinafen / flufenacet combinations on various weed species. As can be seen from the data shown in Table I the
20 application of a combination of picolinafen plus flufenacet gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of either picolinafen alone or flufenacet alone. Crop tolerance (wheat and barley) is excellent for all treatments.

25

Table II gives the results of the postemergence herbicidal activity of picolinafen / carfentrazone-ethyl combinations on *Stellaria media*. As can be seen from the data shown in Table II the application of a combination of picolinafen plus carfentrazone
30 ethyl gives significantly greater weed control than that which could be predicted from the weed control resulting from the application of either picolinafen alone or carfentrazone-ethyl alone. Crop tolerance (wheat and barley) is excellent for all treatments.

35

Table I. Evaluation of the Postemergence Herbicidal Activity of Picolinafen/Flufenacet Combinations

40	Weed Species	Picolinafen (g/ha)	Flufenacet (g/ha)	% Control	
				EXP	OBS
	Galium aparine	15	0	-	78
45		0	15	-	40
		0	30	-	55
		15	15	87	96
		15	30	90	99

	Weed Species	Picolinafen (g/ha)	Flufenacet (g/ha)	% Control	
				EXP	OBS
5	Stellaria media	15	0	-	53
		30	0	-	73
		0	30	-	0
		0	60	-	0
		0	120	-	0
		15	15	87	96
		15	30	53	70
		15	60	53	70
		15	120	73	89
		15	30	60	73
15	30	120	73	92	
15	Alopecurus myosuroides	30	0	-	20
		60	0	-	43
		120	0	-	60
		0	15	-	75
		30	15	80	94
		60	15	86	95
		120	15	90	95
20	Papaver rhoeas	30	0	-	15
		60	0	-	35
		0	15	-	0
		0	30	-	0
		0	120	-	18
		30	15	15	35
		30	30	15	35
		60	15	35	50
		60	30	35	55
		60	120	43	63
30	Lamium pur- purium	30	0	-	15
		0	120	-	18
		30	120	30	58

Table II. Evaluation of the Postemergence Herbicidal Activity of Picolinafen/Carfentrazone-ethyl Combinations on *Stellaria media*

	Picolinafen (g/ha)	Carfentrazone- ethyl (g/ha)	% Control	
			EXP	OBS
40	30	0	-	37
	60	0	-	45
	120	0	-	72
	0	3.75	-	0
	0	7.50	-	0

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	Picolinafen (g/ha)	Carfentrazone- ethyl (g/ha)	% Control	
			EXP	OBS
5	0	15	-	0
	0	30	-	0
10	30	15	37	57
	30	30	37	85
	60	3.75	45	75
	60	7.50	45	91
	60	15	45	67
	60	30	45	85
	120	15	72	80
	120	30	72	91

15 Test Serie B

For the post-emergence treatment, the test plants were first grown to a height of 3 to 20 cm, depending on the growth habit, and only then treated. The herbicides were suspended or emulsified in water as the vehicle and sprayed with the aid of finely distributing nozzles.

Cinidon-ethyl was formulated as a 20 % by weight emulsion concentrate and employed in the spray mixture with addition of that amount of solvent system with which the active ingredient had been applied at the application rates shown in the tables.

Picolinofen was formulated as a 10% by weight emulsion concentrate and employed in the spray mixture with addition of that amount of solvent system with which the active ingredient had been applied at the rates shown in the tables.

The test period extended over 14 days. During this time, the plants were attended, and their responses to the treatments with active ingredients were recorded (Tables III and IV).

Table III: Evaluation of the Postemergence Herbicidal Activity of Picolinafen/Cinidon-ethyl Combinations in spring wheat

	Weed Species (growth stage 14)	Picolinafen (g/ha)	Cinidon- ethyl (g/ha)	% Control	
				EXP	OBS
45	Anthimis	50	-	-	10
	mixta	-	50	-	52
		50	50	57	68
	Veronica	50	-	-	10

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	Weed Species (growth stage 14)	Picolinafen (g/ha)	Cinidon- ethyl (g/ha)	% Control	
				EXP	OBS
5	persicaria	-	50	-	50
		50	50	55	63

Table IV: Evaluation of the Postemergence Herbicidal Activity of Picolinafen/Cinidon-ethyl Combinations in spring barley

10

	Weed Species (growth stage 22)	Picolinafen (g/ha)	Cinidon- ethyl (g/ha)	% Control	
				EXP	OBS
15	Stellaria media	50	-	-	10
		-	50	-	23
		50	50	31	47

20

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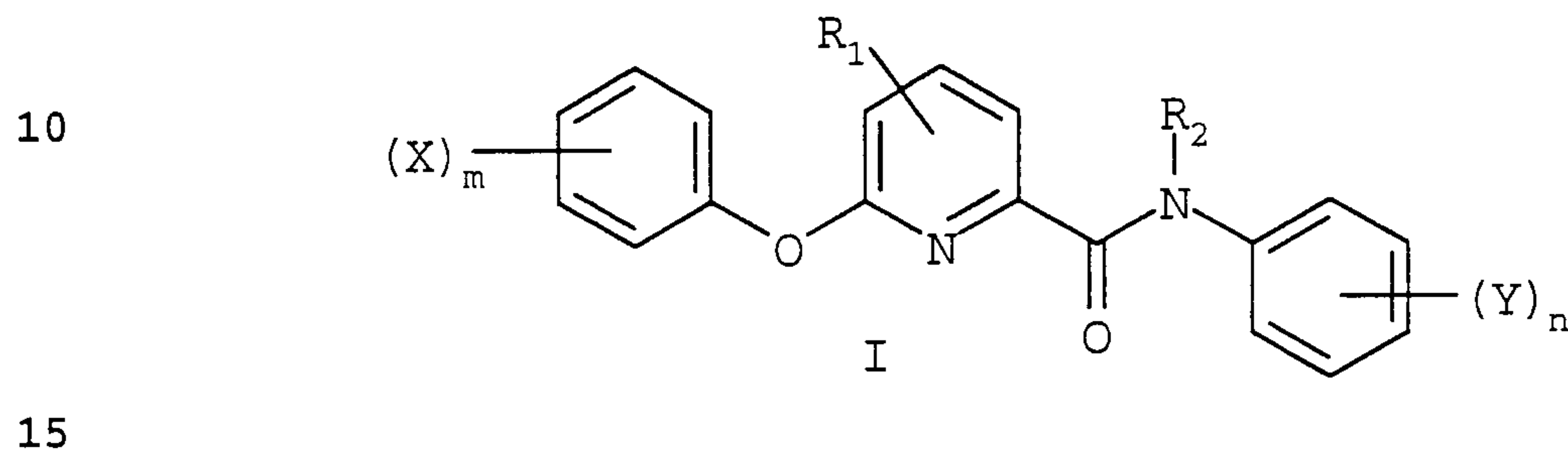
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WHAT IS CLAIMED IS:

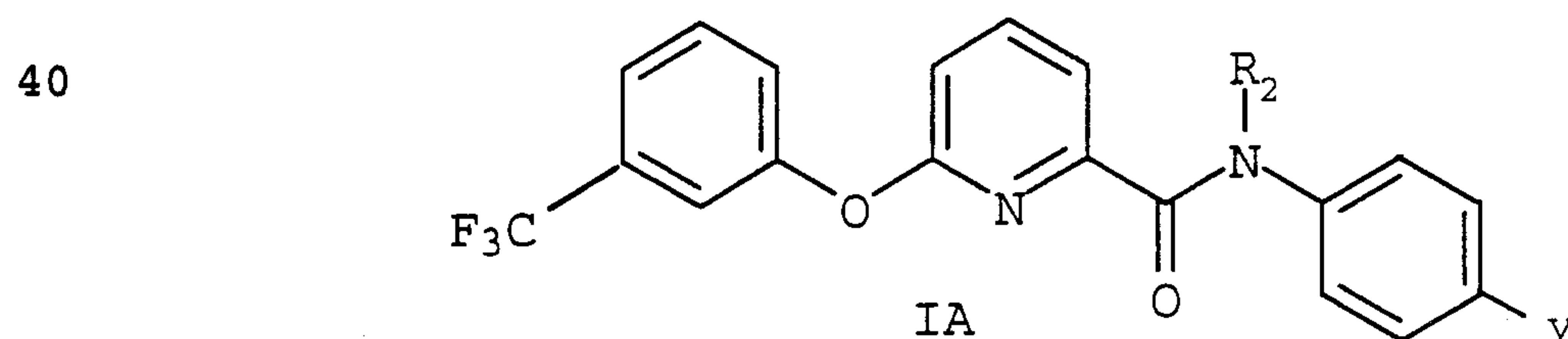
1. A herbicidal composition which comprises an agriculturally acceptable carrier and a herbicidally effective amount of a combination of at least one 6-phenoxy-pyrid-2-ylcarboxamide of formula I



wherein

- 19 R_1 represents a hydrogen or halogen atom or an alkyl or alkoxy group;
- 20 R_2 represents a hydrogen atom or an alkyl group;
- 21 X each independently represents a halogen atom or an optionally substituted alkyl or alkoxy group or, an alkenyloxy, cyano, carboxy, alkoxycarbonyl, (alkylthio)carbonyl, alkylcarbonyl, amido, alkylamido, dialkylamido, nitro, alkylthio, haloalkylthio, alkenylthio, alkynylthio, alkylsulphinyl, alkylsulphonyl, alkyl-oximinoalkyl or alkenyloximinoalkyl group;
- 25 m represents 0 or an integer from 1 to 5;
- 26 Y each independently represents a halogen atom or an alkyl, nitro, cyano, haloalkyl, alkoxy or haloalkoxy group;
- 30 n represents 0 or an integer from 1 to 5; and at least one additional herbicidal compound selected from the group consisting of flufenacet, cinidon-ethyl and carfentrazone-ethyl.

- 35
2. The composition according to claim 1 wherein the 6-phenoxy-pyrid-2-ylcarboxamide has the formula IA

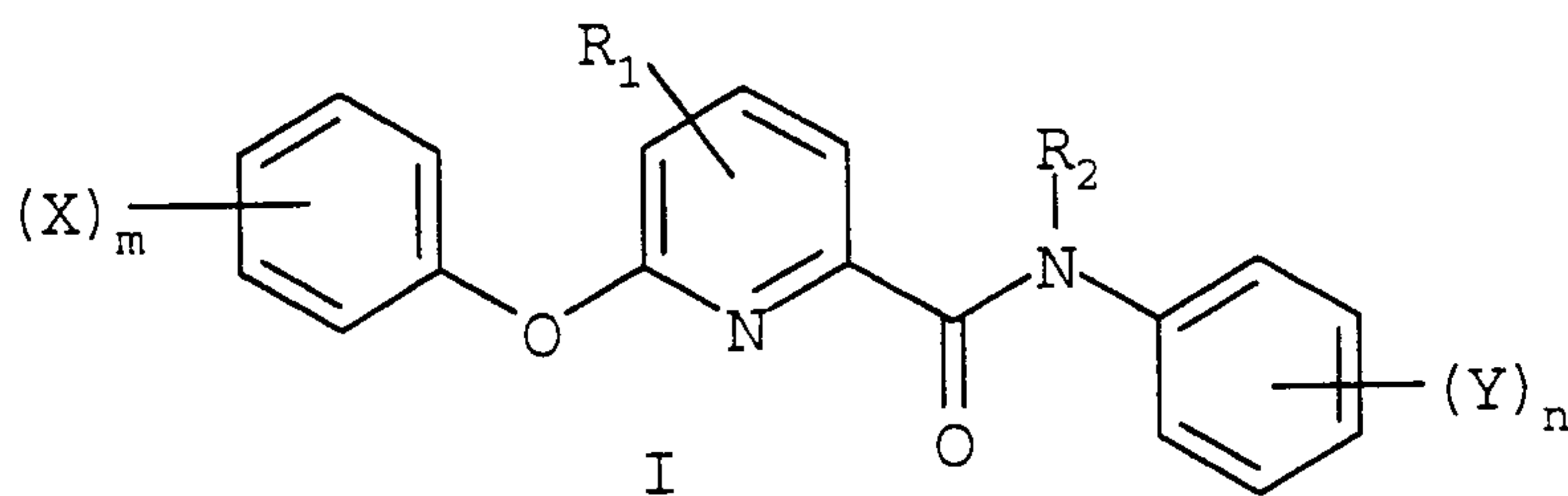


wherein R² and Y are as defined in claim 1.

3. The composition according to claim 2 wherein the 6-phenoxy-pyrid-2-ylcarboxamide is picolinafen.
- 5 4. The composition according to claim 3 wherein said additional herbicidal compound is flufenacet.
- 10 5. The composition according to claim 3 wherein said additional herbicidal compound is cinidon-ethyl.
6. The composition according to claim 3 wherein said additional herbicidal compound is carfentrazone-ethyl.
- 15 7. The composition according to claim 1 wherein the herbicidal composition comprises at least one surfactant.
8. The composition according to claim 7 wherein the 6-phenoxy-pyrid-2-ylcarboxamide is picolinafen and said additional herbicidal compound is cinidon-ethyl.
- 20 9. The composition according to claim 1 wherein the ratio (by weight) of the 6-phenoxy-pyrid-2-ylcarboxamide of formula I to said additional herbicidal compound is from 1000:1 to 1:200.
- 25 10. The composition according to claim 9 wherein the ratio (by weight) of the 6-phenoxy-pyrid-2-ylcarboxamide of formula I to said additional herbicidal compound is from 10:1 to 1:200.
- 30 11. The composition according to claim 9 wherein the ratio (by weight) of the 6-phenoxy-pyrid-2-ylcarboxamide of formula I to said additional herbicidal compound is from 1:1 to 1:80.
- 35 12. The composition according to claim 6 wherein the ratio (by weight) of picolinafen to said additional herbicidal compound cinidon-ethyl is 100:1 to 1:5.
- 40 13. The composition according to claim 6 wherein the ratio (by weight) of picolinafen to said additional herbicidal compound cinidon-ethyl is 10:1 to 1:3,3
- 45 14. A method for the control of undesirable plants which comprises applying to the locus of said plants or to the foliage or stems or seeds of said plants a herbicidally effective

amount of at least one 6-phenoxyppyrid-2-ylcarboxamide of formula I

5



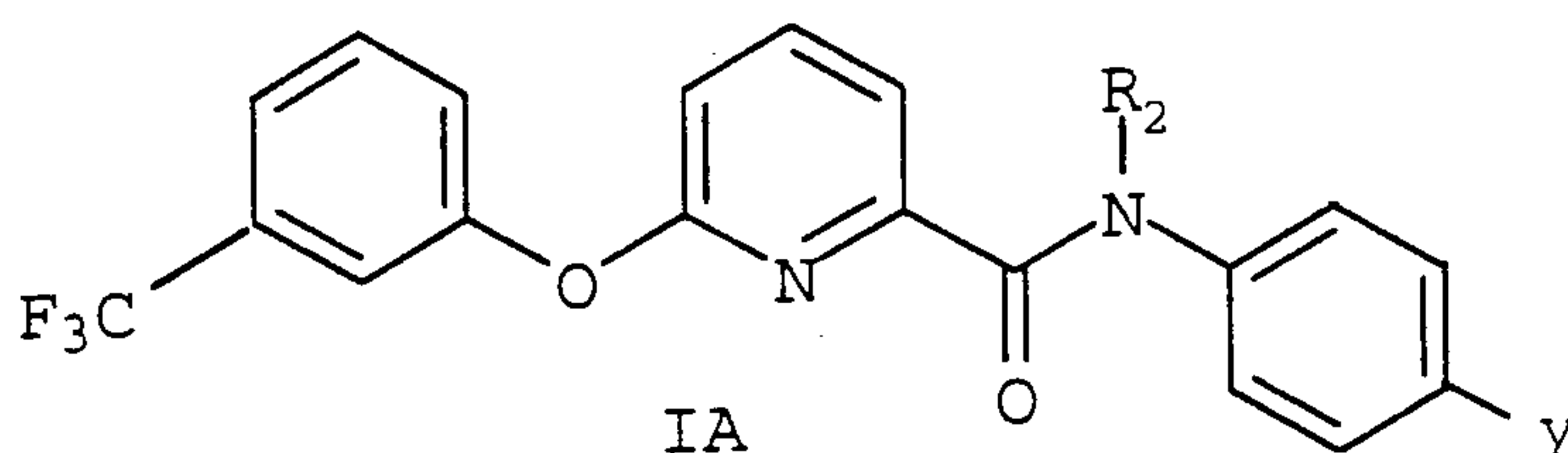
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wherein R^1 , R^2 , X, Y, m and n are as defined in claim 1 and at least one additional herbicidal compound selected from the group consisting of flufenacet, cinidon-ethyl and carfentrazone-ethyl.

15

15. The method according to claim 14 wherein the 6-phenoxyppyrid-2-ylcarboxamide has the formula IA

20



25

30 wherein R^2 and Y are as defined in claim 1.

30

16. The method according to claim 15 wherein the 6-phenoxyppyrid-2-ylcarboxamide is picolinafen.

35 17. The method according to claim 16 wherein said additional herbicidal compound is flufenacet.

18. The method according to claim 16 wherein said additional herbicidal compound is cinidon-ethyl.

40

19. The method according to claim 16 wherein said additional herbicidal compound is carfentrazone-ethyl.

20. The method according to claim 18 wherein the herbicidal composition comprises at least one surfactant.

45

21. The method according to claim 18 which comprises applying picolinafen and cinidon-ethyl - simultaneously or in succession - before, during or after emergence of the undesired plants.
- 5
22. The method according to claim 14, wherein the phenoxy-pyrid-2-ylcarboxamide and the additional herbicidal compound are applied together in a single formulation.
- 10
23. The method according to claim 14, wherein the phenoxy-pyrid-2-ylcarboxamide and the additional herbicidal compound are applied in separate formulations.
- 15
24. The method according to claim 18 wherein picolinafen and cinidon-ethyl are applied together in a single formulation.
25. The method according to claim 18 wherein picolinafen and cinidon-ethyl are applied in separate formulations.
- 20
26. The method according to claim 14 wherein the phenoxy-pyrid-2-ylcarboxamide and the additional herbicidal compound are applied in the presence of a cereal crop plant, crop seed or other crop propagating organ.
- 25
27. The method according to claim 26 wherein the cereal crop is corn, wheat or rice.
28. The method according to claim 26 wherein the cereal crop is wheat.
- 30
29. A method of combating *Alopecurus myosuroides*, *Lolium perenne*, *Setaria viridis*, *Stellaria media*, *Veronica persica*, *Galium aparine*, *Apera spica-venti* and/or *Lamium purpureum* at a locus which comprises applying to the locus a herbicidally effective amount of a composition of claim 1.
- 35
30. A method for the control of dicotyledonous weeds in cereal crops which comprises applying picolinafen and cinidon-ethyl - simultaneously or in succession - before, during or after the emergence of the dicotyledonous weeds.
- 40
31. A method for the control of undesirable plants which comprises treating the leaves of the undesired plants with picolinafen and cinidon-ethyl, either simultaneously or in succession.
- 45

32. A method for the control of dicotyledonous weeds which comprises treating the leaves of the dicotyledonous weeds with picolnafen and cinidon-ethyl, either simultaneously or in succession.

5

33. Method of using the composition according to the invention as claimed in claim 1 for controlling undesired vegetation.

10 34. Method of using the composition according to claim 32 wherein the composition comprises as 6-phenoxyppyrid-2-yl-carboxamide picolnafen and as additional herbicidal compound cinidon-ethyl.

15 35. Method of using the composition according to claim 32 wherein the composition comprises as 6-phenoxyppyrid-2-yl-carboxamide picolnafen and as additional herbicidal compound cinidon-ethyl for controlling undesired vegetation in cereal crops.

20 36. Method of using the composition according to claim 32 wherein the composition comprises as 6-phenoxyppyrid-2-yl-carboxamide picolnafen and as additional herbicidal compound cinidon-ethyl for controlling dicotyledonous weeds.

25 37. Herbicidal agent which is prepared in two parts, the one part comprising picolnafen and an agriculturally acceptable carrier and the other one comprising cinidon-ethyl and an agriculturally acceptable carrier.

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