#### **PCT**

### WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



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

(51) International Patent Classification 6:

(11) International Publication Number:

WO 97/18709

A01N 43/80 // (A01N 43/80, 33:22)

A1 (43) International Publication Date:

29 May 1997 (29.05.97)

(21) International Application Number:

PCT/EP96/04966

(22) International Filing Date:

13 November 1996 (13.11.96)

(30) Priority Data:

9523724.4

20 November 1995 (20.11.95) GB

(71) Applicant (for all designated States except US): RHONE-POULENC AGROCHIMIE [FR/FR]; 14-20, rue Pierre-Baizet, F-69009 Lyon (FR).

(72) Inventors; and

- (75) Inventors/Applicants (for US only): LEROUX, Bernard [FR/FR]; 13, allée Vaubecour, Chazay, F-69380 Lozanne (FR). RONSSIN, Sylvie [FR/FR]; 21, avenue du Point-du-Jour, F-69005 Lyon (FR).
- (74) Agent: BRACHOTTE, Charles; Rhône-Poulenc Agrochimie D.P.I., Boîte postale 9163, F-69263 Lyon Cédex 09 (FR).

(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

#### **Published**

With international search report.

(54) Title: NEW HERBICIDAL COMPOSITIONS CONTAINING 4-BENZOYLISOXAZOLES AND ACLONIFEN

$$\begin{array}{c|c} R & O \\ \hline & & \\ N & O \\ \hline & & \\ R^1 & & \\ \hline & & \\ R^2)_n & \end{array}$$
 (I)

#### (57) Abstract

The invention relates to compositions comprising: (a) a 4-benzoylisoxazole of formula (I) wherein R is hydrogen or  $-CO_2R^3$ ;  $R^1$  is cyclopropyl;  $R^2$  is selected from halogen,  $-S(O)_pMe$  and  $C_{1-6}$  alkyl or haloalkyl; n is two or three; p is zero, one or two; and  $R^3$  is  $C_{1-4}$  alkyl; and (b) 2-chloro-6-nitro-3-phenoxyaniline, which is aclonifen; and to their use as herbicides.

#### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
ΑU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL.	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic	SD	Sudan
CF	Central African Republic		of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

#### NEW HERBICIDAL COMPOSITIONS CONTAINING 4-BENZOYLISOXAZOLES AND ACLONIFEN

This invention relates to a new method for controlling weeds and to the compositions used in this method.

5

Aclonifen (2-chloro-6-nitro-3-phenoxyaniline) is a known herbicide (see for example U.S. Patent No. 4,394,159) used preemergence to control grasses and broad-leaved weeds in a number of crops, including maize.

10

Herbicidal 4-benzoylisoxazoles are disclosed in the literature, see for example European Patent Publication Nos. 0418175, 0487357, 0527036 and 0560482. In particular, the compound 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethyl-benzoyl)isoxazole has been disclosed as having good pre-emergence control of grasses and broadleaved weeds in maize (Vrabel et al., Proc. N. Cent. Weed Sci. Soc., 1994, 49).

15

As a result of research and experimentation it has now been discovered that the use of certain 4-benzoylisoxazole derivatives in combination with aclonifen add to its capabilities of controlling a wide spectrum of broad-leaf weeds, grasses and sedges.

20

25

In addition to this it has been found that the combined herbicidal activity of combinations of 4-benzoylisoxazole derivatives with aclonifen against certain species is greater than expected, i.e. the herbicidal activity of combinations of 4-benzoylisoxazole derivatives with aclonifen showed on unexpected degree of synergism, as defined either by P.M.L. Tammes, Netherlands Journal of Plant Pathology, 70 (1964), pp 73-80 in a paper entitled "Isoboles, a graphic representation of synergism in pesticides"; or by Limpel, L.E., P.H. Schuldt and D. Lamont, 1962, 1. Proc. NEWCC 16, 48-53, using the formula:-

 $E = X + Y - \underline{X.Y}$ 

30

(also known as the Colby formula) where:

E = the expected percent inhibition of growth by a mixture of two herbicides A and B at defined doses.

35

X = the percent inhibition of growth by herbicide A at a defined dose.

Y = the percent inhibition of growth by herbicide B at a defined dose.

When the observed percentage of inhibition by the mixture is

greater than the expected value E using the formula above the combination is synergistic.

The remarkable synergistic effect gives improved reliability of control of a number of weed species and allows for a reduction in the amount of active ingredients employed.

A high level of control of these weeds is desirable to prevent:-

- 1) yield loss, through competition and/or difficulties with harvest,
- 2) crop contamination leading to storage and cleaning difficulties, and
  - 3) unacceptable weed seed return to the soil.

The present invention therefore provides a method for the control of weeds at a locus which comprises applying to the locus:

(a) a 4-benzoylisoxazole of formula (I):

$$R \underset{O}{ \longrightarrow} (R^2)_n$$

15

5

10

wherein

R is hydrogen or  $-CO_2R^3$ ;

R<sup>1</sup> is cyclopropyl;

20

 $R^2$  is selected from halogen,  $-S(O)_pMe$  and  $C_{1-6}$  alkyl or haloalkyl (e.g. trifluoromethyl);

n is two or three; p is zero, one or two; and

 $\mathbb{R}^3$  is  $\mathbb{C}_{1-4}$  alkyl; and

(b) 2-chloro-6-nitro-3-phenoxyaniline, which is aclonifen.

25

For this purpose, the 4-benzoylisoxazole herbicide and aclonifen are normally used in the form of herbicidal compositions (i.e. in association with compatible diluents or carriers and/or surface-active agents suitable for use in herbicidal compositions), for example as hereinafter described.

30

In formula (I) above, compounds in which n is three and the groups  $(R^2)_n$  occupy the 2, 3 and 4-positions of the benzoyl ring; or in which n is two and the groups  $(R^2)_n$  occupy the 2- and 4- positions of the benzoyl ring are preferred.

In formula (I) above, preferably one of the groups R<sup>2</sup> is

WO 97/18709 PCT/EP96/04966

3

 $-S(O)_pMe$ .

R is preferably hydrogen, methoxycarbonyl or ethoxycarbonyl (especially hydrogen). Compounds of formula (I) in which  $(R^2)_n$  is 2-SO<sub>2</sub>Me-4-CF<sub>3</sub> are also preferred.

5

The 4-benzoylisoxazole of formula (I) of particular interest in combination with aclonifen is 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethyl)benzoylisozaxole, hereafter referred to as compound A.

The amounts of the 4-benzoylisoxazole herbicide and aclonifen

10

time of application, the climatic and edaphic conditions and (when used to control the growth of weeds in crop-growing areas) the nature of the crops. When applied to a crop-growing area, the rate of application

applied vary with the nature of the weeds, the compositions used, the

15

should be sufficient to control the growth of weeds without causing substantial permanent damage to the crop. In general, taking these factors into account, application rates from 1g to 500g of the 4-benzoylisoxazole and from 30g to 2500g of aclonifen per hectare give

4-benzoylisoxazole and from 500g to 2500g of aclonifen per hectare. However, it is to be understood that higher or lower application rates may be used, depending upon the particular problem of weed control

good results, more preferably from 10g to 200g of the

20

encountered.

25

The 4-benzoylisoxazole herbicide and aclonifen in combination may be used to control selectively the growth of weeds, for example to control the growth of those species hereinafter mentioned, by preemergence application in a directional or non-directional fashion e.g. by

30

directional or non-directional spraying, to a locus of weed infestation which is an area used, or to be used, for growing crops, for example wheat, barley, oats, rye, maize and rice, soya beans, field and dwarf beans, peas, lucerne, cotton, peanuts, flax, onions, carrots, oilseed rape, sunflower, sugarcane, potatoes and permanent or sown grassland before

or after sowing of the crop or before or after emergence of the crop.

By the term 'pre-emergence application' (pre-em) 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' (post-em) is meant application to the aerial or exposed portions of the weeds which have emerged above the surface of the soil. By the term 'early post-emergence application' (early

post) is meant application to the aerial or exposed portions of the weeds

WO 97/18709 PCT/EP96/04966

which have emerged above the surface of the soil and are between the cotyledonous stage and the second to third leaf stage (or third and fourth whorl stage) of growth.

For the selective control of weeds at a locus of weed infestation which is an area used, or to be used, for the growing of various crops under various conditions the following application rates of the 4-benzoylisoxazole and aclonifen (referred to in the Table below as 'Isox' and 'Aclo' respectively) per hectare are particularly suitable:

Dose Rate of active ingredient (in g/ha)

			Dose Rate	ı g/ha)			
		Pro	Preferred		Preferred	Especially preferred	
Crop	Appln.	Isox	Aclo	Isox	Aclo	Isox	Aclo
Maize	Pre-em	30 - 150	500-1000	30 - 100	500-1000	35 - 75	ca 500
Winter cereal	Early post or post-em	25 - 200	500-1500	100 - 150	500-1500	100-150	500 -
Spring cereal	Pre-em, early post or post-em	10 - 100	500-1500	10 - 50	500-1500	ca 20	500 - 1500
Potato	Pre-em	10 - 100	1500-2500	20 - 50	1500- 2500	ca 20	1500 - 2000
Sugar- cane	Pre-em	35 - 200	500 - 1000	75 - 150	500-1500	ca 75	ca 500
···	Early post	35 - 150	500 - 1000	50 - 100	500-1000	ca 75	ca 500
	Post-em	35 - 150	500 - 1000	50 - 100	500-1000	ca 75	ca 500

10

5

Due to selectivity properties of the combination, the use of the 4benzoylisoxazole herbicide and aclonifen for the control of weeds in potatoes, maize or sugarcane is preferred, most preferably preemergence.

15

20

The mixtures of the present invention may also be used to control the growth of weeds at loci which are not crop-growing areas but in which the control of weeds is nevertheless desirable. Examples of such non-crop-growing areas include airfields, industrial sites, railways, roadside verges, the verges of rivers, irrigation and other waterways, scrublands and fallow or uncultivated land, in particular where it is desired to control the growth of weeds in order to reduce fire risks.

5

10

15

20

25

30

5

When used for such purposes in which a total herbicidal effect is frequently desired, the active compounds are normally applied at dosage rates higher than those used in crop-growing areas as hereinbefore described. The precise dosage will depend upon the nature of the vegetation treated and the effect sought. In general, dose rates of from 150 g to 500 g per hectare of the 4-benzoylisoxazole herbicide and from 1500 to 2500 g per hectare of aclonifen are used.

The use of the mixture to control weeds in areas to be used for the growth of certain crops (e.g. potatoes), at the dose rates described above for the use in non-crop growing areas is also a feature of the invention.

The following non-limiting examples illustrate the invention.

#### Example A1

The following experiments were conducted pre-emergence of the weed and crop species at a field research centre in France in May (soil type:- silt clay with 33% sand, 42% silt and 22% clay and a pH of 7.6). Compound A (formulated as a wettable powder) and aclonifen (formulated as a suspension concentrate) were dissolved in water and sprayed either alone or in mixture at various dose rates at a spray volume of 400 l/ha to 26.5 square metre field plots which had been sown 1 day earlier with the various plant seeds. Three replicates were performed and the percentage phytotoxicity was assessed 39 days after treatment (26 days for the crop species) expressed as a percentage damage in comparison with an untreated control. In the tables that follow the figures in brackets represent the expected value according to the Colby formula.

## RESULTS Table A1 Panicum milliaceum

Aclonifen

Compound A

Dose (g/ha)	0	500	1000
0	-	<u>-</u>	7.5
50	32.5	67.5	85.0(37.6)
100	87.0	84.0	97.0(88.4)
150	99.0	90.0	100(99.1)

Table A2 Setaria viridis

# Aclonifen

#### Compound A

Dose (g/ha)	0	500	1000
0	-	-	10.0
50	57.5	85.0	89.5(61.8)
100	87.0	90.0	95.0(84.3)
150	97.0	97.5	100(97.3)

Table A3 Maize (Zea Mays: variety: SABRINA)

#### Aclonifen

#### Compound A

5

Dose (g/ha)	0	500	1000
0	-	<u>-</u>	0
50	0	0	0
100	0	0	0
150	0	1	0

#### Example A2 (Glasshouse experiment)

Seed of the various species of broad-leaf or grass weeds were sown in unsterilised clay loam soil in 7 centimetre by 7 centimetre plastic plant pots. The pots were watered and allowed to drain. The soil surface was then sprayed with ranges of concentrations of either the individual herbicide or mixtures of two herbicides in various proportions, dissolved in a 50:50 by volume solution of acetone and water, using a track sprayer set to deliver the equivalent of 290 l/ha. All herbicides were used as unformulated technical materials.

Treated pots were placed at random in four replicate blocks per treatment for each plant species. The pots were held, in a glasshouse, standing on moist capillary matting, under lights and with overhead watering twice daily. Two weeks after treatment the percent reduction in plant growth, compared to an untreated control, was assessed.

Mean percent reduction in plant growth was calculated for each treatment. Dose/mean response was plotted on Log concentration/Probability graph paper, and lines fitted by eye. For herbicide mixtures a dose/response line for the first herbicide was drawn for each dose rate of the second herbicide and a dose/response line for the second herbicide was drawn for each dose rate of the first herbicide.

20

15

10

PCT/EP96/04966

7

The doses representing a 90% reduction in plant growth (ED90's) were read from these lines and plotted on graphs whose axes were dose rates of the two herbicides. The line joining these points is an Isobole i.e. a line joining points (mixtures) of equal activity, as described by P.M.L. Tammes, Neth. J. Plant Path. 70 (1964): 73-80. A line was also drawn joining the ED90 values of the individual components when applied alone. This line represents the theoretical isobole if the effect of the two components is additive i.e. there is no interaction between them. Isoboles falling below this line indicate synergy between the components while lines lying above it indicate antagonism.

In the tables that follow 'dose' represents the dose rate in grammes per hectare of the active ingredient used; and the figures for the weed control are percentages reduction in growth when compared with the untreated controls.

5

WO 97/18709

#### **RESULTS:**

#### Table B1

Pre-emergence treatment of Digitaria sanguinalis with various mixtures of compound A and Aclonifen.

5

	Aclonifen										
Dose g/ha	0	31.25	62.5	125	250	500	1000	2000			
0		12.5	7.5	21.25	90	92.5	99.5	99.5			
1	0	20	17.5	61	75	98.75	98.25	99.5			
2	7.5	22.5	41.25	50	81	98.5	99.5	99.75			
4	23.75	38.75	51.66	58.75	97.25	99.75	99.5	98.5			
8	25	35	61.25	85	98.75	99.75	99.75	100			
16	80	87.5	83.5	92.5	92.5	99.75	99.75	100			
32	77.25	94.75	76	97.25	97.25	99.75	99.5	100			
64	79.25	82	97.25	98.5	99.5	99.75	99.75	99.75			
128	94.75	99.5	99.75	99.75	99.5	99.5	99.25	100			
256	100	99.25	73.5	99.75	99.75	99.75	99.75	100			

Cpd A

## Table B2 Pre-emergence treatment of Setaria faberi with various mixtures of compound A and Aclonifen.

Aclonifen

Dose g/ha	0	31.25	62.5	125	250	500	1000	2000
0	<u> </u>	12.5	23.75	43.33	71.25	87.25	94.75	96.25
1	2.5	18.75	17.5	38.75	72.5	88.75	96	97.25
2	30	12.5	17.5	43.75	52.5	77.5	96	100
4	11.25	15	30	52.5	58.75	88.75	96.25	93.75
8	0	26.25	23.75	35	83.75	96.25	96	97.5
16	47.5	40	23.75	47.5	82.5	95	98.75	99.75
32	21.25	51.25	43.75	62.5	86.25	96	98.75	98.5
64	65	86.25	47.5	93.75	78.75	98.5	97	98.25
128	73.5	91.25	71.25	84.5	82.5	97	97.25	99.25
256	97	93.5	87.25	87	96.75	99.25	99.75	99

Cpd A

Table B3

Pre-emergence treatment of Setaria viridis with various mixtures of compound A and Aclonifen.

Actomica									
Dose g/ha	0	31.25	62.5	125	250	500	1000	2000	
0	-	12.5	5	31.25	57.5	82.5	85	100	
1	23.75	12.5	5	25	92.5	97.5	99.75	97.5	
2	36.67	32.5	0	32.5	71.25	86.25	99.75	100	
4	43.75	20	13.75	48.75	71.25	91.25	98.75	99.5	
8	10	17.5	35	50	65	77.5	93.75	99.75	
16	72.5	45	61.25	61.25	92.5	96.25	97.5	100	
32	88.75	82.5	63.75	75	86.67	93.75	99.5	97.5	
64	75	81	77.5	98.75	99.5	96.25	96	99.75	
128	87.5	74.5	97.25	93.75	99.75	98.75	100	99.75	
256	95	97.5	99.5	98.75	100	99.75	100	100	

Aclonifen

Cpd A

#### **Brief Description of Drawings**

Figure I is an ED90 plot calculated from observed values (-•-) and a corresponding plot of expected additive values for the mixtures of compound A with aclonifen against the weed species <u>Digitaria</u> sanguinalis.

10

5

Figure II is an ED90 plot calculated from observed values (-•-) and a corresponding plot of expected additive values for the mixtures of compound A with aclonifen against the weed species <u>Setaria faberi</u>.

15

Figure III is an ED90 plot calculated from observed values (-•-) and a corresponding plot of expected additive values for the mixtures of compound A with aclonifen against the weed species <u>Setaria viridis</u>.

The isoboles produced from the data in Tables B1, B2 and B3 shown in Figs. I to III hereafter, were clearly type III curves (Tammes, op. cit., Page 75, Fig 2), characteristic of synergism.

20

25

#### Example A3

The following tests were carried out pre-emergence of the weed species at a research farm in Essex, England in a sand silt loam type soil. Compound A (formulated as a 75% wettable dispersible granule) and aclonifen (formulated as a suspension concentrate) were dissolved in water and either sprayed alone or in a tank mix at various dose rates to plots of 10 square metre size which had been sown 2 days earlier with the various plant seeds. Three replicates were performed. The results were assessed 53 days after treatment by visual comparison of the

WO 97/18709 PCT/EP96/04966

10

percentage phytoxicity in comparison with an untreated control.

#### **RESULTS**

5

10

15

20

Table C1	Galium aparine						
•		Aclonif	en				
	Dose (g/ha)	0	2100				
	0	-	43				
Compound A	10	0	97(43)				
	20	0	90(43)				
	30	0	77(43)				

#### <u>Table C2</u> <u>Solanum nigrum</u>

Aclonifen

 Dose (g/ha)
 0
 2100

 0
 7

 Compound A
 10
 38
 65(42)

 20
 95
 97(95)

 30
 100
 100(100)

<u>Table C3</u> <u>Polygonum convolvulus</u>

Aclonifen

 Dose (g/ha)
 0
 2100

 0
 52

 10
 17
 97(60)

 20
 43
 98(73)

 30
 25
 75(64)

#### Example A4

The following experiments were conducted pre-emergence of the crop, potatoes (Solanum tuberatum) at research centres in France, Spain and the United Kingdom in sandy loam soil during the normal growing season for potatoes. Compound A (formulated as a wettable powder and aclonifen (formulated as a suspension concentrate) were dissolved in water and sprayed either alone or in tank mixtures at various dose rates at a spray volume of 300 - 400 l/ha to 15 square metre plots which had been sown 2 days earlier with potatoes. Three replicates were performed and the percentage phytoxicity and efficacy was assessed 55, 56 or 64

WO 97/18709 PCT/EP96/04966

11

days after treatment (in France, Spain and the United Kingdom respectively) in comparison with an untreated control.

#### Results

5

Table D1

Active Ingredient	Amount	Percentage phytotoxicity				
	(g/ha)	France	Spain	UK		
Cpd A	27	0	0	0		
Cpd A	40	0	0	0		
Cpd A	53	0	0	0		
Aclonifen	2100	0	0	0		
Aclonifen	4200	0	0	0		
Cpd A + Aclonifen	27+2100	0	0	0		
Cpd A + Aclonifen	30+4200	0	0	0		
Cpd A + Aclonifen	53+2100	0	0	0		
Cpd A + Aclonifen	80+4200	0	0	0		

#### Example A5

10

15

The following test was conducted at a Brazilian research farm (soil content: clay 29%; silt 9.6%; sand 61%) using the same materials and procedure as describe in Example A4 above, except that in this case the herbicides were applied early post-emergence of the plants. The growth stages of the plants when the herbicides were applied were as follows:

Panicum maximum (1-3 cm), Brachiaria plantaginea (0.5 -1cm), and sugar cane (5-10 cm). The sugarcane used was ratoon cane, and the percentage phytotoxicity was assessed at 14 and 56 days after treatment (DAT). The results were as follows (note that in the Table the figures in brackets represent the expected percentage phytotoxicity for the weed species according to the Colby formula). The experiment also included a standard mixture used for controlling weed found in sugarcane (hexazinone +diuron).

20

#### Results

Table E1

Active ingredient	DOSE (g ai/ha)	Sugarcane (14DAT)	Panicum maximum (14DAT)	Panicum maximum (56DAT)	Brachiaria plantaginea (14DAT)	Brachiaria plantaginea (56DAT)
Cpd A	52	7	27	23	20	15
Cpd A	75	12	60	47	50	28
Aclonifen	1000	7	20	10	22	10
Aclonifen	1500	7	33	12	33	12
Cpd A + Aclonifen	52+1000	14	93(42)	92 (31)	92(38)	92 (23)
Cpd A + Aclonifen	52+1500	14	95(51)	93 (32)	93(46)	93(25)
Cpd A + Aclonifen	75+1000	14	95(68)	93(52)	93(61)	93(35)
Hexazinone + Diuron	330+1170	8	85	53	93	92

5

According to a further feature of the present invention, there are provided herbicidal compositions comprising:

(a) a 4-benzoylisoxazole derivative of formula I as defined above; and

#### (b) aclonifen:

10

15

in association with, and preferably homogeneously dispersed in, one or more compatible herbicidally- acceptable diluents or carriers and/or surface-active agents (i.e. diluents or carriers or surface-active agents of the type generally acceptable in the art as being suitable for use in herbicidal compositions and which are compatible with aclonifen and 4-benzoylisoxazole derivatives). The term "homogeneously dispersed" is used to include compositions in which aclonifen and 4-benzoylisoxazole derivatives are dissolved in the other components. The term "herbicidal composition" is used in a broad sense to include not only compositions which are ready for use as herbicides but also concentrates which must be diluted before use.

20

The compositions preferably comprise (a) 4-benzoylisoxazole derivative and (b) aclonifen in proportions of from 1:2500 to 16.7:1, preferably from 1:250 to 1:2.5 wt/wt of (a):(b).

Preferably, the compositions contain from 0.05 to 90% by weight of aclonifen and 4-benzoylisoxazole derivative(s).

The herbicidal compositions may contain both a diluent or carrier

5

10

15

20

25

30

35

and a surface-active (e.g. wetting, dispersing, or emulsifying) agent. Surface-active agents which may be present in herbicidal compositions of the present invention may be of the ionic or non-ionic types, for example sulphoricinoleates, products based on condensates of ethylene oxide with nonyl- or octyl-phenols, or carboxylic acid esters of anhydrosorbitols which have been rendered soluble by etherification of the free hydroxy groups by condensation with ethylene oxide, alkali and alkaline earth metal salts or sulphuric acid esters and sulphonic acids such as dinonyl- and dioctyl-sodium sulphono-succinates and alkali and alkaline earth metal salts of high molecular weight sulphonic acid derivatives such as sodium and calcium lignosulphonates. Examples of suitable solid diluents or carriers are aluminium silicate, talc, calcined magnesia, kieselguhr, tricalcium phosphate, powdered cork, absorbent carbon black and clays such as kaolin and bentonite. The solid compositions (which may take the form of dusts, granules or wettable powders) are preferably prepared by grinding aclonifen and the 4benzoylisoxazole derivative with solid diluents or by impregnating the solid diluents or carriers with solutions of aclonifen and 4benzoylisoxazole derivative in volatile solvents, evaporating the solvents and, if necessary, grinding the products so as to obtain powders. Granular formulations may be prepared by absorbing aclonifen and the 4-benzoylisoxazole derivative (dissolved in volatile solvents) onto the solid diluents or carriers in granular form and evaporating the solvents, or by granulating compositions in powder form obtained as described above. Solid herbicidal compositions, particularly wettable powders, may contain wetting or dispersing agents (for example of the types described above), which may also, when solid, serve as diluents or carriers.

Liquid compositions according to the invention may take the form of aqueous-organic solutions, suspensions and emulsions which may incorporate a surface-active agent. Suitable liquid diluents for incorporation in the liquid compositions include water, acetophenone, cyclohexanone, isophorone, toluene, xylene and mineral, animal and vegetable oils (and mixtures of these diluents). Surface-active agents, which may be present in the liquid compositions, may be ionic or non-ionic (for example of the types described above) and may, when liquid, also serve as diluents or carriers.

Wettable powders and liquid compositions in the form of

WO 97/18709

14.

PCT/EP96/04966

concentrates may be diluted with water or other suitable diluents, for example mineral or vegetable oils, particularly in the case of liquid concentrates in which the diluent or carrier is an oil, to give compositions ready for use. When desired, liquid compositions of aclonifen and 4-benzoylisoxazole derivative may be used in the form of self-emulsifying concentrates containing the active substances dissolved in the emulsifying agents compatible with the active substances, the simple addition of water to such concentrates producing compositions ready for use.

10

5

Liquid concentrates in which the diluent or carrier is an oil may be used without further dilution using the electrostatic spray technique.

Herbicidal compositions according to the present invention may also contain, if desired, conventional adjuvants such as adhesives, protective colloids, thickeners, penetrating agents, stabilisers, sequestering agents, anti-caking agents, colouring agents and corrosion inhibitors. These adjuvants may also serve as carriers or diluents.

Preferred herbicidal compositions according to the present invention are in the form of aqueous suspension concentrates; wettable powders; liquid water soluble concentrates; liquid emulsifiable suspension concentrates; granules or emulsifiable concentrates.

20

15

In addition the compositions may be provided in the form of a gel. This is particularly useful where the composition is intended for packaging in a water soluble bag, for example as described in European Patent Publication Nos. 0577702 and 0608340, and U.S Patent Nos. 5,222,595; 5224,601; 5,351,831; and 5,323,906.

25

The processes described in European Patent Publication Nos. 0418175, 0487357, 0527036 and 0560482 may be used to prepare the compounds of formula (I).

30

Herbicidal compositions according to the present invention may also comprise aclonifen and 4-benzoylisoxazole derivative in association with, and preferably homogeneously dispersed in, one or more other pesticidally active compounds and, if desired, one or more compatible pesticidally acceptable diluents or carriers, surface-active agents or conventional adjuvants as hereinbefore described. Preferred partners with the combination of the present invention include diflufenican, bromoxynil, atrazine, and isoproturon.

35

Pesticidally active compounds and other biologically active materials which may be included in, or used in conjunction with, the

WO 97/18709 PCT/EP96/04966

15

herbicidal compositions of the present invention, for example those hereinbefore mentioned, and which are acids, may, if desired, be utilised in the form of conventional derivatives, for example alkali metal and amine salts and esters.

5

The following non-limting Example illustrates compositions according to the invention. In the description that follows the following trademarks appear:- Moret, Soprophor, Antimousse, Rhodopol, Proxel.

#### 10 Example B1

A suspension concentrate was prepared containing the following ingredients:

Compound A:	78g	Aclonifen	510g
Propylene glycol	50g	Moret D423	50g
Soprophor PB60	20g	Antimousse 432	5g
Citric acid	1.5g	Rhodopol 23	2g
Proxel GXL	1g	Water	462.5g.

Similar suspension concentrates may be prepared by replacing the isoxazole (Compound A) with other isoxazoles of formula (I).

20

25

15

According to a further feature of the present invention, there is provided a product comprising:

- (a) a 4-benzoylisoxazole derivative of general formula I above; and
  - (b) aclonifen;

as a combined preparation for simultaneous, separate or sequential use, for example, in controlling the growth of weeds at a crop locus.

5

10

15

20

25

#### **CLAIMS**

- 1. A method for the control of weeds at a locus which comprises applying to the locus a herbicidally effective amount of:
  - (a) a 4-benzoylisoxazole of formula (I):

$$\begin{array}{c|c}
R & O \\
N & R^{1} & R^{2} \\
\hline
(I)
\end{array}$$

wherein

R is hydrogen or -CO<sub>2</sub>R<sup>3</sup>;

R<sup>1</sup> is cyclopropyl;

 $R^2$  is selected from halogen,  $-S(O)_pMe$  and  $C_{1-6}$  alkyl or haloalkyl;

n is two or three; p is zero, one or two; and

 $R^3$  is  $C_{1-4}$  alkyl; and

(b) 2-chloro-6-nitro-3-phenoxyaniline, which is aclonifen.

- 2. The method according to claim 1 in which one of the groups  $R^2$  is  $-S(O)_pMe$ , wherein p is as defined in claim 1.
- 3. The method according to claim 1 or 2 in which R is hydrogen, methoxycarbonyl or ethoxycarbonyl.
  - 4. The method according to claim 1, 2 or 3 in which  $(R^2)_n$  is 2-SO<sub>2</sub>Me-4-CF<sub>3</sub>.
  - 5. The method according to any one of the preceding claims in which the 4-benzoylisoxazole of formula (I) is 5-cyclopropyl-4-(2-methylsulphonyl-4-trifluoromethyl)benzoylisozaxole.
- 30 6. The method according to any one of the preceding claims using from 1g to 500g per hectare of the 4-benzoylisoxazole and from 30g to 2500g of aclonifen per hectare.
  - 7. The method according to any one of the preceding claims

PCT/EP96/04966

5

10

15

25

in which the locus is an area used, or to be used, for the growing of a crop.

- 8. The method according to claim 7 in which the crop is selected from maize, sugarcane and potatoes.
  - 9. A herbicidal composition comprising:
  - (a) a 4-benzoylisoxazole derivative of formula I as defined in any one of claims 1 to 5; and
  - (b) 2-chloro-6-nitro-3-phenoxyaniline, which is aclonifen; in association with one or more compatible herbicidally acceptable diluents or carriers or a surface-active agent.
  - 10. A composition according to claim 9 in which the weight ratio of (a): (b) is from 1:2500 to 16.7:1.
  - 11. A composition according to claim 9 in which the weight ratio of (a): (b) is from 1:250 to 1:2.5.
- 20 12. A product comprising:
  - (a) a 4-benzoylisoxazole derivative of general formula I as defined in claim 1, 2 or 3; and
  - (b) 2-chloro-6-nitro-3-phenoxyaniline, which is aclonifen; as a combined preparation for simultaneous, separate or sequential use in controlling the growth of weeds at a locus.

FIG I

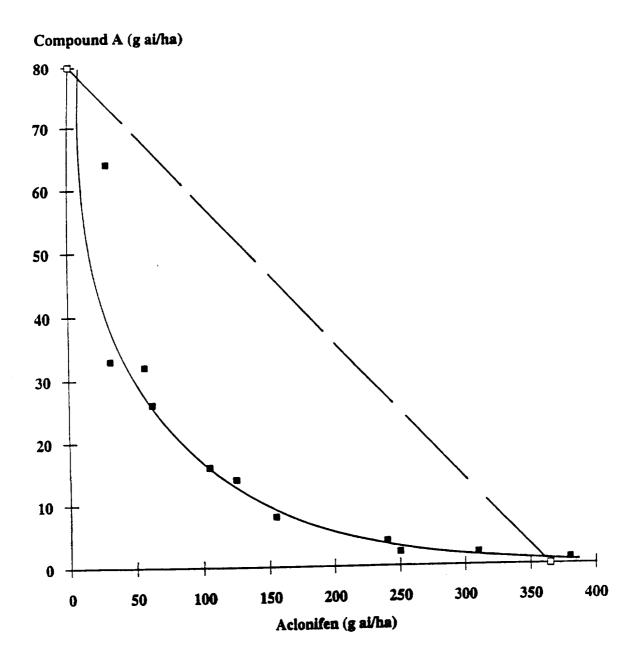


FIG II

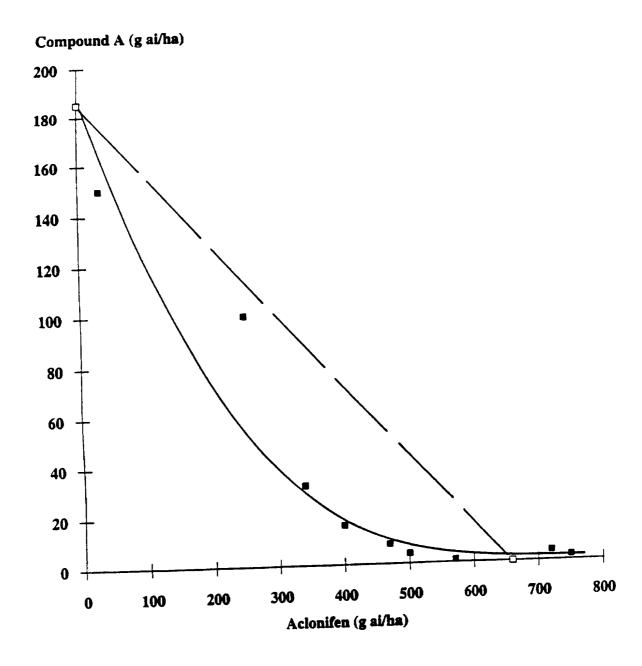
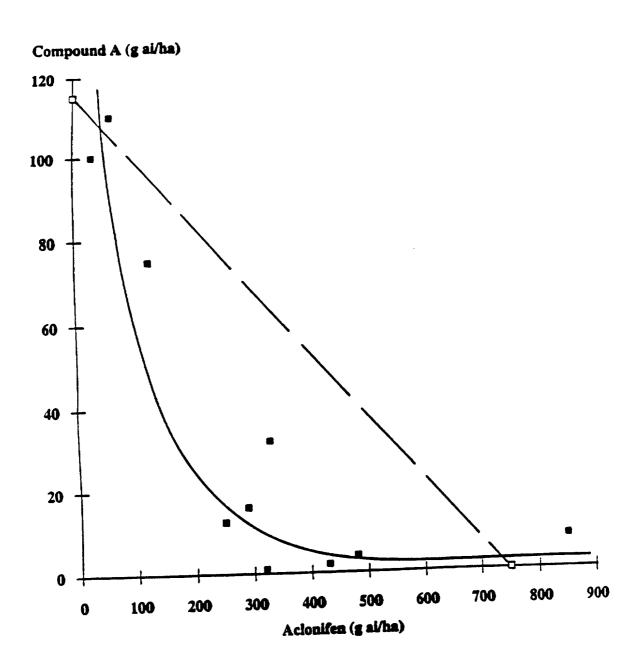


FIG III



## INTERNATIONAL SEARCH REPORT

Internation No PC., EP 96/04966

A. CLASSI IPC 6	FICATION OF SUBJECT MATTER A01N43/80 //(A01N43/80,33:22)		
<b>A</b>	o International Patent Classification (IPC) or to both national classif	ication and IPC	
B. FIELDS	s SEARCHED locumentation searched (classification system followed by classificati	on symbols)	
IPC 6	A01N		
Documental	tion searched other than minimum documentation to the extent that s	such documents are included in the fields se	arched
Electronic d	iata base consulted during the international search (name of data bas	e and, where practical, search terms used)	
C. DOCUN	MENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the re	elevant passages	Relevant to claim No.
A	EP 0 527 036 A (RHONE POULENC AGRICULTURE) 10 February 1993 cited in the application see page 2, line 21 see page 10, line 27 - line 38		1-12
Α	GB 2 284 547 A (RHONE POULENC AGRICULTURE) 14 June 1995 see the whole document		1-12
А	FR 2 656 985 A (RHONE POULENC AGROCHIMIE) 19 July 1991 see the whole document		1-12
Fu	rther documents are listed in the continuation of box C.	X Patent family members are listed	in annex.
*Special categories of cited documents:  *A* document defining the general state of the art which is not considered to be of particular relevance  *E* earlier document but published on or after the international filing date  *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  *O* document referring to an oral disclosure, use, exhibition or other means  *P* document published prior to the international filing date but  *C* document published prior to the international filing date but  *C* document published prior to the international filing date but  *C* document published prior to the international filing date but  *C* document published prior to the international filing date but  *C* 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  *C* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined with one or more other such document is combined to involve an inventive and invention cannot be considered to involve an inventive and invention ca			
later	earch report		
	26 February 1997	5.03.1997	
	i mailing address of the ISA  European Patent Office, P.B. 5818 Patentlaan 2	Authorized officer	
	NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Far (+31-70) 340-3016	Lamers, W	

#### INTERNATIONAL SEARCH REPORT

isormation on patent family members

Inter onal Application No PC., EP 96/04966

	·	PC./E	P 96/04966
Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0527036 A	10-02-93	AT 144981 T AU 655648 B AU 2073092 A BG 96747 A CA 2075348 A CN 1069268 A DE 69215028 D EG 19908 A ES 2094878 T HR 920256 A IL 102675 A JP 5202008 A NZ 243817 A SK 241292 A ZA 9205872 A	15-11-96 05-01-95 11-02-93 24-03-94 06-02-93 24-02-93 12-12-96 31-05-96 01-02-97 31-10-95 31-10-96 10-08-93 24-02-95 08-02-95 01-03-93
GB 2284547 A	14-06-95	AU 1312295 A CN 1137221 A WO 9515691 A EP 0732876 A PL 314961 A SK 74196 A	27-06-95 04-12-96 15-06-95 25-09-96 30-09-96 06-11-96
FR 2656985 A	19-07-91	FR 2656769 A AT 4491 A,B AU 635599 B AU 6924991 A BE 1005340 A CA 2033481 A CH 682204 A DE 4100702 A ES 2033570 B FR 2656983 A FR 2656984 A GB 2241892 A,B GR 1000823 B IT 1244366 B JP 4217901 A LU 87872 A NL 9100029 A	12-07-91 15-08-93 25-03-93 18-07-91 29-06-93 12-07-91 13-08-93 18-07-91 16-01-94 19-07-91 19-07-91 18-09-91 25-01-93 08-07-94 07-08-92 01-08-91

#### INTERNATIONAL SEARCH REPORT

isormation on patent family members

Internanal Application No PC1/EP 96/04966

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2656985 A	·	SE 9100017 A	12-07-91
•			
			(
			!