PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A01N 25/30 — A1

(11) International Publication Number: WO 95/03697

(43) International Publication Date: 9 February 1995 (09.02.95)

(21) International Application Number: PCT/FI94/00331

(22) International Filing Date: 27 July 1994 (27.07.94)

(30) Priority Data:
933374 28 July 1993 (28.07.93) FI

(71) Applicant *(for all designated States except US)*: KEMIRA OY [FI/FI]; P.O Box 44, FIN-02271 Espoo (FI).

(72) Inventors; and

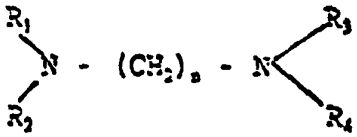
(75) Inventors/Applicants *(for US only)*: HARJU-JEANTY, Pontus [FI/FI]; Almantie 24, FIN-65610 Mustasaari (FI). JUPPO, Ari [FI/FI]; Isolahdentie 4 A 6, FIN-65210 Vaasa (FI). AHLSKOG, Torbjörn [FI/FI]; Vapaudentie 38 As. 18, FIN-65200 Vaasa (FI). JOKINEN, Kari [FI/FI]; Ulvilantie 20 E 62, FIN-00350 Helsinki (FI).

(74) Agent: BERGGREN OY AB; P.O. Box 16, FIN-00101 Helsinki (FI).

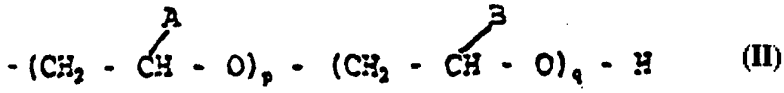
(81) Designated States: BG, BY, CA, CZ, FI, JP, KZ, LT, LV, NO, PL, RO, RU, SI, SK, UA, US, UZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: HERBICIDE COMPOSITION, ACTIVITY-PROMOTING AGENT FOR IMPROVING THE EFFICACY OF THE HERBICIDE, AND A METHOD FOR TREATING CULTIVATED PLANTS



(I)



(II)

(57) Abstract

A herbicide composition comprising one or more active ingredients, known per se, such as benzofuran, bipyridine, hydroxybenzonitrile, carbamoyl phenyl carbamate, pyridazine, quinoline, sulphonyl urea or triazine herbicide, and one or more activity-promoting agents for improving the efficacy of the active ingredient/ingredients. According to the invention, the herbicide comprises at least one activity-promoting agent which is tetraalkoxylated alkyl diamine with general formula (I) in which R_1, R_2, R_3 and R^4 are groups which, independent of each other, conform to formula (II), in which one of groups A and B is hydrogen and the other a lower alkyl group, and p+q = 5-150, and n = 1-6, whereby the molecular weight of the compound according to formula (I) is in the range of about 1 000-40 000.

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.

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

HERBICIDE COMPOSITION, ACTIVITY-PROMOTING AGENT FOR IMPROVING THE EFFICACY OF THE HERBICIDE, AND A METHOD FOR TREATING CULTIVATED PLANTS

This invention relates to a herbicide composition comprising at least one or more active ingredients, known per se, such as bipyridine, hydroxybenzonitrile, carbamoyl phenyl carbamate, pyridazine, quinoline, sulphonyl urea, or triazine herbicides, and one or more activity-promoting agents for improving the efficacy of the active ingredient/ingredients. The invention further relates to a method for treating plantations such as sugar beet plantations and the like, using a herbicide, and to an activity-promoting agent for increasing the efficacy of the active ingredient of the herbicide, such as benzofuran, bipyridine, hydroxybenzonitrile, carbamoyl phenyl carbamate, pyridazine, quinoline, sulphonyl urea, or triazine active ingredients.

The efficacy of foliage-applied herbicides can be improved by surface-active additives which decrease the surface tension of the herbicides, affording more even spreading of sprayed drops on the surfaces of the leaves thus increasing the area of contact between the herbicide and the leaf surface. Owing to their wax-dissolving properties, lipophilic surface-active additives can also be used to provide more effective penetration of herbicides. Hydrophilic surface-active agents can be used to improve the translocation inside plants.

Traditionally, water-insoluble active ingredients have been formulated into emulsion concentrates, and active ingredients insoluble in organic solvents into wettable powders. However, both of these formulations are very user-unfriendly because of the toxicity and flammability of the solvents, and problems with packaging materials and storage. Wettable powders are problematic because of the heavy dust formation.

Because of the above-described problems, there has been a general attempt to shift to more user-friendly suspensions or granules suspended in water. However, the active ingredients in

these are in the form of solid particles, unlike in emulsion concentrates where they are in the form of dissolved molecules, whereby the biological efficacy generally suffers because bigger particles do not penetrate into plants as well as molecules do.

Because of the above, the insoluble active ingredient particles have to be ground into powder of maximum fineness and their penetration and translocation properties improved by activity-promoting agents such as oils, organic solvent additives and/or surface-active agents. Especially, when using herbicides containing carbamoyl phenyl carbamate, it is necessary to add exceptionally large amounts of these additives in order to achieve sufficient biological efficacy.

Grinding is carried out using air jet mills and suspension mills in order to provide active ingredients of maximum fineness, preferably in the order of 1-5 microns, to ensure the biological effect. Fineness is also required to provide permanent suspensions, improved storage stability of suspension concentrates and improved suspension properties for suspended granules.

English patent publication GB 998264, for instance, shows that ethoxylated fatty amines improve the absorption of certain herbicides, such as paraquat and glyphosate, to the leaves. However, ethoxylated fatty amines carry the significant disadvantage of gelling in water, whereby their capability of dissolving the surface waxes of leaves is reduced and the penetration of herbicides is not optimal. On the other hand, increase of the amount of surface-active agents may promote phytotoxic characteristics which damage the host plant. In addition, these ethoxylated fatty amines are extremely hydrophilic, whereby the property brought along by lipophilicity, i.e. enhanced penetration of the herbicide through the wax layer of the leaf, is lacking. Hydrophilic surface-active agents such as fatty amines are thus mainly suitable only as additives to hydrophilic active ingredients such as paraquat and glyphosate.

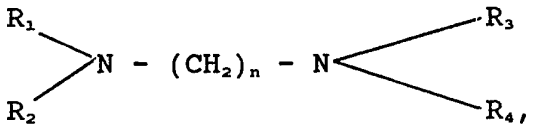
It is further known from European patent publication EP 0 257 686 that ethoxy propoxy monoamines can improve the biological efficacy of herbicides. The fatty amines or fatty amido amines/imidazolines formed by this activity-promoting agent contain at least one higher 8-22 C radical connected to one or more nitrogen atoms. The molecular weight of the activity-promoting agent should be less than 2500.

International patent application WO 91/13546 further teaches how to use ethoxy propoxylated block copolymers in the form of water-soluble thermoactive binding agents, as additives for granulation.

EP application publication 417 896 discloses a pesticide composition comprising of a water-insoluble pesticide and a surface-active agent. The surface-active agent consists of polyethoxylated poly(ethylene amine) and the ester of polyol and C_{16}-C_{22}-unsaturated aliphatic acid.

The purpose of the present invention is to provide an improved herbicide composition.

The purpose of the present invention is especially to provide an improved activity-promoting agent for enhancing the efficacy of the active ingredient of a herbicide. In order to achieve the above objects, the herbicide composition according to the invention is characterized in that the herbicide comprises at least one activity-promoting agent which is tetraalkoxylated alkyl diamine. The efficacy of the activity-promoting agent can be advantageously improved in a synergetic way by means of ethoxy propoxy block copolymer. Surprisingly, it has thus been found that tetraalkoxylated alkyl diamines, the general formula of which is:



in which n = 1-6,

R_1, R_2, R_3 and R_4 = - $(CH_2\text{-}\overset{A}{C}H\text{-}O)_p$ - $(CH_2\text{-}\overset{B}{C}H\text{-}O)_q$ - H,
p+q = 5-150,

and in which one of the compositions A or B is a hydrogen and the other a methyl or an ethyl group, and the molecular weight of which is about 1 000 - 40 000, considerably increase the biological efficacy of the previously mentioned benzofuran, bipyridine, hydroxybenzonitrile, carbamoyl phenyl carbamate, pyridazine, quinoline, sulphonyl urea, and triazine herbicides on weeds.

The above-mentioned activity-promoting agents are surface-active agents which have been found to have an exceptional property of increasing the biological efficacy of benzofuran, bipyridine, hydroxybenzonitrile, carbamoyl phenyl carbamate, pyridazine, quinoline, sulphonyl urea, and triazine herbicides generally clearly more so than other surface-active agents used in connection with herbicides usually do. It has been further found that these and some other surface-active agents act synergetically, increasing the biological efficacy of the herbicides in question more than expected of these surface-active agents additively.

The alkoxylated diamines according to the invention have proven to be especially effective in improving the efficacy of herbicides on harmful weeds such as lamb's quarters or fathen (Chenopodium album), bistort (Polygonum spp.), mayweed (Matricaria inodorum), bedstraw (Galium spurium) and rape (Brassica napus).

The molecular weight of the activity-promoting agent according to the invention is preferably 4 000 - 25 000, whereby the size of the molecule does not limit its efficacy, especially on lamb's quarters or fathen.

At the same time, it has been found that ethoxylated propoxylated block copolymers, the molecular weights of which are about 2 000 - 20 000, preferably 10 000 - 18 000, act synergetically with tetraalkoxylated alkyl diamines on rape

(Brassica napus), which represents weeds having a considerable layer of wax on the surfaces of their leaves. The hydrophilicity and biological effect of these block copolymers on rape increases with the weight of the molecule. Thus it is probable, on the one hand, that the lipophilicity of the tetraalkoxylated alkyl diamines according to the invention dissolves the surface wax of leaves and increases penetration and, on the other hand, that the hydrophilicity of the ethoxy propoxy block copolymers further increases penetration/translocation.

The activity-promoting agents according to the invention, i.e., tetraalkoxylated diamines and ethoxy propoxylated block copolymers, which both increase the biological efficacy of said active ingredients, can be added into a spray tank as separate activity-promoting tank-mixtures or preferably included in the formulation itself. If the herbicide used is in liquid form, the promoting agents can be mixed with the liquid phase. When using solid herbicides, liquid promoting agents can be absorbed into carriers and those in solid form can be introduced directly into the herbicide mass. The activity-promoting agents can be in the form of separate granules in solid herbicides or they can be incorporated in the same granules with the active ingredients of the herbicides.

The herbicides according to the invention are otherwise formulated in a conventional way. The active ingredients are dissolved in water or organic solvents, suspended in a carrier liquid, or formulated into a solid form. They generally contain about 5-80% of active ingredients. Water, oil, or mixtures of water and oil are generally used as carrier liquids in suspension concentrates. Surface-active agents (anionic, cationic, non-ionic or ampholytic) are used to provide and improve emulsifiability, dispersibility, suspension stability, wettability, penetration and translocation, and to emulsify the oil in the actual concentrate, and to provide miscibility and suspension/emulsion stability in the final dilution. The preparations can include other additives such as water-miscible and/or water-soluble carriers and/or deflocculation agents such as kaolin or lignin compounds, anti-foam agents (for instance,

silicone-based agents), thickening agents such as cellulose derivatives, anti-freeze agents in water suspension such as propylene glycol, organic solvents such as kerosine, and colouring agents. In addition, preservatives such as formalin can be used, especially if the preparation contains organic suspending or thickening agents. In the case of wettable granules and pellets, inert inorganic (for instance, silicic acid, salts) or organic (for instance, cellulose, polyacrylates, urea) compounds can be used as carriers to dilute the active ingredients or to adsorb liquid agents.

The active ingredients of herbicide formulations in solid form are advantageously very fine ground, less than 10μm, preferably 1-3μm. Grinding of dry matter is carried out using an air jet mill, for instance, and that of suspensions using a bead mill. The formulation of suspension concentrates is carried out in a reactor using effective agitation, and the granules or pellets are manufactured by known techniques, for instance, by utilizing disc granulation, spray drying, fluidized bed granulation, mixing granulation using a vertical mixer or a blade mixer, and extrusion, compacting, centrifugal, spraying-bed or spraying/cooling granulations.

The weight ratio of the amounts of activity-promoting agents to the amounts of active ingredients in the formulations is, for instance, from 15:1 to 1:2, preferably from 5:1 to 1:1. An optimal weight ratio of alkoxylated diamine to ethoxy propoxy block copolymer in a rape-spray is from 1:2 to 1:4. However, in a lamb's quarters or fathen-spray it is more preferable to use a larger amount of alkoxylated diamine. Thus the weight ratio can range in lamb's quarters or fathen-sprays preferably from 10:1 to 1:10.

In addition to the above, other biocides as well as fertilizers can be mixed with the suspension concentrate, granule/pellet, or final dilution. The other biocides include, for instance, other herbicides such as acetamide, diphenyl ether, organophosphorus, pyridine, thiocarbamate, triazine, and uracil herbicides, plant disease control agents, insecticides, and growth regulators. In

order to increase the spectrum of control, it is preferable to use for sugar beet and the like, in particular, substances such as lenacil, metolachlor, trichlor acetic acid, EPTC, cycloate, clopyralide, fluroxypyr, benzthiazuron, chlorpropham, fenuron, isocarbimide, propham, trifluralin, alloxydimsodium, sethoxydim, cycloxydim, diallate, fluazifob-butyl, triallate, dalapon, propaquizafop, diclofop-methyl, fenoxaprop-ethyl, quizalofop-ethyl, haloxyfopethoxy ethyl, and proximpham in addition to the above-mentioned agents.

The invention is described in more detail in the following with the aid of examples.

The biological efficacy of herbicides was determined in a greenhouse by means of pot tests. Steady temperature, humidity and lighting conditions were maintained in the greenhouse by automatic means. Generally, the test plants included weeds which cause a lot of harm on sugar beet plantations and the like, such as lamb's quarters or fathen (Chenopodium album = C. album), and rape (Brassica napus = B. napus) which deviate from each other with respect to the surface morphology of their leaves and thus represent different types of weed. The tests also employed Mercurialis annua (= M. annua) when testing benzofuran herbicides, mayweed, i.e., Matricaria inodorum (= M. inodorum), which is sensitive to triazines and pyridazines; black bindweed, i.e., Polygonum convolvulus (= P. convolvulus) was used for testing bipyridines, hydroxybenzonitriles and sulphonyl ureas, and bedstraw, i.e., Galium spurium (= G. spurium) for quinolines and sulphonyl ureas. The susceptibility of cultivated plants to herbicidal injury was determined using seedlings of sugar beet (Beta vulgaris).

The tests generally employed 5-8 seedlings per plant-pot and 3-5 pots in parallel. The amount of water was 200 l/ha, and application was carried out with an automatic dosing sprayer when the weeds were at about the 2-leaf stage. The final estimate on the efficacy of the herbicide was made 13-15 days after the spraying.

In the results below, the efficacy is expressed as the dry or

fresh weight of the above-ground parts of the weeds or cultivated plants per pot or per seedling.

EXAMPLE 1

The test can be used to show that the alkoxylated diamine (molecular weight MW=6700) according to the invention is clearly more effective than previously known ethoxylated tallow fatty acid amines (EO 15, 20 and 30).

The suspension of active ingredient was prepared from 80% phenmedipham granules suspended in water. The diamine according to the invention as well as the tallow fatty acid amines were mixed as tank mixture additives to the suspension of active ingredient.

Amount of phenmedipham = 720 g/ha

Activity-promoting agent	Amount used kg/ha	Dry matter g/pot C.album	B.napus
1. Without prom.agent	-	2.1	2.4
2. Alkoxylated diamine (MW=6700)	1	0.6	1.6
3. Ethoxylated tallow fatty acid amine (EO=15)	1	1.2	2.1
4. Ethoxylated tallow fatty acid amine (EO=20)	1	1.3	2.0
5. Ethoxylated tallow fatty acid amine (EO=30)	1	1.1	2.4
6. Commercial preparation Armoblen T/25, ethoxylated tallow fatty acid amine (EO=15)	1	1.3	2.0

EXAMPLE 2

Different alkoxylated diamines (MW = 3 600, 6 700, 7 500 and 12 000) were studied by the test. The efficacy was found to improve when the molecular weight was over 3 600, and some kind of optimum was reached when the molecular weight was about 7 000.

Amount of phenmedipham = 720 g/ha
Preparation of the spray as in EXAMPLE 1.

Activity-promoting agent	Amount used kg/ha	Dry matter g/pot	
		C.album	B.napus
1. Without prom.agent	-	2.7	2.8
2. Alkoxylated diamine (MW=3600)	1	1.3	1.9
3. Alkoxylated diamine (MW=6700)	1	0.8	1.5
4. Alkoxylated diamine (MW=7500)	1	0.9	1.7
5. Alkoxylated diamine (MW=12000)	1	1.1	1.7

EXAMPLE 3

The test indicated that both 1 kg/ha alkoxylated diamine (MW=6700) and 1 kg/ha ethoxy propoxy block copolymer (MW=4150) yield a level of efficacy which can not be improved much further on B.napus, even if the dosages are doubled. The alkoxylated diamine (MW=6700) was more effective than the ethoxy propoxy block copolymer (MW=4150), especially on Chenopodium album, and synergy on Brassica napus was observed with a mixture of 20% + 80% (alkoxylated diamine + ethoxy propoxy block copolymer). The mixture of alkoxylated diamine and ethoxy propoxy block copolymer was more effective than a corresponding mixture of ethoxylated tallow fatty acid amine and ethoxy propoxy block copolymer. The alkoxylated diamine (MW=6700) was more effective than the ethoxy propoxy block copolymer, especially against

Chenopodium album.

Amount of phenmedipham = 720 g/ha.
Preparation of the spray as in EXAMPLE 1.

Activity-promoting agent	Amount used kg/ha	Dry matter g/pot C.album	B.napus
1. Without prom.agent	-	2.7	2.8
2. Alkoxylated diamine	0.2	1.5	2.4
3. Alkoxylated diamine	1.0	1.4	2.1
4. Alkoxylated diamine	2.0	0.8	2.1
5. EO-PO block copolymer	0.2	1.3	2.6
6. EO-PO block copolymer	1.0	1.4	2.1
7. EO-PO block copolymer	2.0	1.3	2.0
8. Alkoxylated diamine	0.2	1.4	1.9
EO-PO block copolymer	0.8		
9. Alkoxylated diamine	0.5	1.2	2.1
EO-PO block copolymer	0.5		
10. Alkoxylated diamine	0.8	1.0	2.2
EO-PO block copolymer	0.2		
11. Alkoxylated diamine	0.2	1.4	2.1
+ EO tallow fatty acid amine	0.8		
12. EO-PO monoamine	1	1.7	2.1

EXAMPLE 4

The test indicated that the mixture of alkoxylated diamine (MW= 6 700) and ethoxy propoxy copolymer (MW=14 000) was synergetic, especially on Brassica napus. This test also showed that ethoxylated tallow fatty acid amine (EO=15) was less effective than alkoxylated diamines.

Amount of phenmedipham = 720 g/ha.
Preparation of the spray as in EXAMPLE 1.

Activity-promoting agent	Amount used kg/ha	Dry matter g/pot C.album	B.napus
1. Without prom.agent	-	1.6	2.2
2. Alkoxylated diamine (MW=6700)	1	0.4	1.5
3. EO-PO block copolymer (MW=14000)	1	0.6	1.0
4. EO-PO block copolymer (MW=14000) 75% + alkoxylated diamine (MW=6700) 25%	1	0.4	0.9
5. Ethoxylated tallow fatty acid amine (EO=15)	1	0.8	1.7

EXAMPLE 5

The test indicated that the molecular weight of ethoxy propoxy block copolymers had no appreciable significance regarding efficacy.

Amount of phenmedipham = 720 g/ha.
Preparation of the spray as in EXAMPLE 1.

Activity-promoting agent	Amount used kg/ha	Dry matter g/pot C.album	B.napus
1. Without prom.agent	-	1.9	2.4
2. EO-PO block copolymer (MW=6600)	1	0.8	1.6
3. EO-PO block copolymer (MW=12500)	1	0.8	1.4
4. EO-PO block copolymer (MW=14000)	1	0.8	1.5
5. EO-PO block copolymer (MW=14000)	0.7	0.8	1.2
+ alkoxylated diamine (MW=6700)	0.2		
+ dispersing agent	0.1		

EXAMPLE 6

The test indicated that the activity-promoting granule according to the invention, consisting of 70% ethoxy propoxy block copolymer, 20% alkoxylated diamine and 10% dispersing agent, enhances the action of ethofumesate and metamitron to a considerable extent. The test also indicated that the activity-promoting granule has a clearly better effect than a conventional oil emulsifier activity-promoting tank-additive, named Actipron (RP) as a commercial preparation, on the weeds studied (Chenopodium album, Matricaria inodorum, Mercurialis annua). However, the active ingredient metamitron has no effect on Mercurialis annua.

Preparation	Active ingredient (g/ha)
Ethofumesate 70% WG	400
Metamitron 80% WG (Goltix/Bayer)	360
Ethofumesate 20% EC (Kemiron/Kemira)	400

Preparation of the spray as in EXAMPLE 1.

Preparation	Activity-prom. granule kg/ha	Fresh weight (g/seedling) C.album	M.inodorum	M.annua
1. Untreated	-	1.400	1.176	0.938
2. "	0.1	1.263	0.955	0.814
3. "	0.5	1.350	0.938	1.028
4. "	1.0	1.345	0.948	1.033
5. "	2.0	1.323	0.979	1.034
6. Ethofumesate EC	-	0.890	1.002	0.485
7. Ethofumesate WG	-	1.183	1.039	0.473
8. "	0.1	1.071	0.899	0.475
9. "	0.5	0.783	0.902	0.380
10. "	1.0	0.680	0.960	0.405
11. "	2.0	0.675	0.817	0.384
12. Metamitron	-	1.286	0.357	0.917
13. "	0.1	0.898	0.334	0.916
14. "	0.5	0.468	0.178	0.982
15. "	1.0	0.382	0.256	1.016
16 "	2.0	0.478	0.157	0.962

References Actipron (l/ha)				
17. Ethofumesate WG	1.0	0.940	0.936	0.415
18. Metamitron WG	1.0	0.865	0.429	1.000

EXAMPLE 7

The test indicates that
- there is no appreciable further increase in the enhancing effect of the activity-promoting granule when the amount used exceeds 1 kg/ha,
- the emulsifying oil incorporated in the activity-promoting granule improves the efficacy further, especially against Chenopodium album,
- the ethoxy propoxy monoamine as a tank mixture additive does not increase the efficacy of the activity-promoting granule on Chenopodium album and that it has an antagonistic, efficacy-reducing effect on Brassica napus.

Amount of phenmedipham = 720 g/ha 80% of the phenmedipham granule and amount of activity-promoting agent = 1 or 2 kg/ha of the activity-promoting granule.

Activity-promoting agent	Used amount kg/ha	Dry matter g/pot C.album	B.napus
1. Untreated	-	1.9	2.4
2. EO-PO block copolymer	0.7	0.8	1.2
+ alkoxylated diamine	0.2		
+ dispersing agent	0.1		
3. EO-PO block copolymer	1.4	0.8	1.0
+ alkoxylated diamine	0.4		
+ dispersing agent	0.2		
4. EO-PO block copolymer	1.2	0.6	0.8
+ alkoxylated diamine	0.4		
+ vegetable oil	0.36		
+ dispersing agent	0.04		

5. EO-PO block copolymer	1.4	0.7	1.7
+ alkoxylated diamine	0.4		
+ dispersing agent	0.2		
+ EO-PO monoamine	1.0		

EXAMPLE 8

The test investigated the behaviour of a three-part mixture, consisting of phenmedipham (8%) + ethofumesate (10%) + metamitron (20%), in combination with an activity-promoting agent according to the invention. The results indicate that the mixture of alkoxylated diamine and ethoxy propoxy block copolymer is synergetic. The optimal weight ratio of the mixture, considering both weeds (C. album and B. napus), is about 2:7. The ethoxy propoxy monoamine tested was clearly less effective than the mixture of diamine and ethoxy propoxy block copolymer on both weeds.

The amounts of active ingredients were: phenmedipham 150 g/ha, ethofumesate 190 g/ha and metamitron 180 g/ha. The active ingredient granules were suspended in water 200 l/ha and the activity-promoting agents were added in the form of either granules or liquid.

Activity-promoting agent	Amount used kg/ha	Dry matter (mg/ seedling)	
		C.album	B.napus
1. Untreated	-	430	390
2. Without prom.agent	-	290	380
3. EO-PO block copolymer	0.9	80	240
+ dispersing agent	0.1		
4. Alkoxylated diamine	0.2	60	170
+ EO-PO block copolymer	0.7		
+ dispersing agent	0.1		
5. Alkoxylated diamine	0.45	40	270
+ EO-PO block copolymer	0.45		
+ dispersing agent	0.1		
6. EO-PO monoamine	1	170	280

EXAMPLE 9

A separate ethoxy propoxy monoamine tank mixture additive does not further enhance the action of the granules of a three-part mixture consisting of phenmedipham (8%) + ethofumesate (10%) + metamitron (20%) and complemented with activity-promoting granules of the optimal mixture of alkoxylated diamine and ethoxy propoxy block copolymer (2:7). In fact, a clearly antagonistic effect is obtained on Brassica napus.

Amounts of active ingredients:

phenmedipham	150 g/ha
ethofumesate	190 g/ha
metamitron	380 g/ha

The granules of the active ingredients were suspended in water, 200 l/ha, and the ethoxy propoxy monoamine was added in liquid form separately to the spraying dilution at 1 kg/ha.

Activity-promoting agent	Amount used kg/ha	Dry matter g/pot C.album	B.napus
1. Untreated	-	1.9	2.4
2. Alkoxylated diamine	0.2	0.2	0.8
+ EO-PO block copolymer	0.7		
+ dispersing agent	0.1		
3. Alkoxylated diamine	0.2	0.2	1.3
+ EO-PO block copolymer	0.7		
+ dispersing agent	0.1		
+ EO-PO monoamine	1.0		

EXAMPLE 10

The test compared a product according to the invention and three products already on the market for efficacy on weeds. At the same time, their effects on host plants were compared. In each case, the active ingredients in the final dilutions were in the form of solid particles of a few microns in size, and the end product was either in solid form granule WG suspendable in

water, or as suspension concentrate SC. The preparation according to the invention contained as activity-promoting agents 10% alkoxylated diamine + 35% ethoxy propoxy block copolymer, corresponding to 0.1 kg diamine and 0.35 kg block copolymer per hectare.

The total amount of active ingredients in all the cases was 360 g/ha and the amount of water 200 l/ha.

The test indicated that the preparation according to the invention has a clearly better efficacy than competing products on both frostblite, i.e., Chenopodium album, and rape, i.e., Brassica napus, and that damage to the host plant, which was sugar beet, i.e., Beta vulgaris, is insignificant with all the products studied.

Preparation	Active ingredient g/ha	Dry matter g/pot		
		C.album	B.napus	B.vulgaris
1. Untreated	-	2.3	2.6	3.0
2. WG according to the invention - phenmedipham 8% - ethofumesate 10% - metamitron 20% including an activity-promoting agent according to the invention	360	0.4	1.4	2.9
3. Commercial WG Goltix Triple/Bayer - phenmedipham 6.5% - ethofumesate 6.5% - metamitron 28%	360	0.9	1.8	2.9
4. Commercial SC Betanal Trio SC/Schering - phenmedipham 5% - ethofumesate 5% - metamitron 15%	360	0.6	1.6	3.2
5. Commercial SC Mentor Star SC/Plüss-Stauffer	360	1.2	2.6	2.9

- phenmedipham 9.2%
- ethofumesate 9.2%
- metamitron 27.1%

EXAMPLE 11

The test compared the efficacy of an activity-promoting granule according to the invention with that of a commercial tallow fatty acid amine activity-promoting agent (Armoblen T/25) and a commercial oil-emulsifying activity-promoting agent (Actipron) in different herbicides. Suitable weeds were selected for the herbicides in question.

The activity-promoting granule according to the invention consisted of 70% EO-PO block copolymer, 20% alkoxylated diamine and 10% dispersing agent.

The studied herbicides by chemical family, their active ingredients, preparation names and dosages were as follows:

Chemical family	Active ingredient	Preparation	Dosage of preparation/ ha
Bipyridine	Diquat dibromide	Reglone	0.75 l
Hydroxybenzo-nitrile	Bromoxynil	80% WG	0.1875 kg
Pyridazine	Chloridazon	Pyramin FL	3.0 kg
	Pyridate	Lentagran	2.0 kg
Quinoline	Quinmerac	BAS 51802H	2.0 kg
Sulphonyl urea	Triasulphuron	Logran	0.02 kg

The test may be used to show that the solid activity-promoting granule according to the invention improves the biological efficacy of the preparations mentioned in the example at least as well as the control liquid activity-promoting agents Armoblen T/25 and Actipron do when the active ingredient is bromoxynil, chloridazone or triasulphuron. The actions of the other active ingredients are markedly enhanced by the solid activity-improving granule according to the invention as compared with

mixtures without activity-promoting agent, and almost as well as by liquid activity-promoting agents.

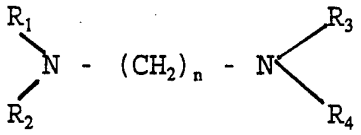
The spraying mixtures were prepared by mixing the preparations in the above-mentioned amounts with an amount of water corresponding to 200 l/ha, and 1 kg of activity-promoting granule, 1 l of Armoblen T/25 or 1 l of Actipron per hectare was added as the activity-promoting agent.

	Dry matter (mg/seedling) Black bindweed (P.convolvulus)		
	Bipyridine (Diquat dibromide)	Sulphonyl urea (Triasulphuron)	Hydroxy-benzo-nitrile (Bromoxynil)
1. Untreated	726	744	619
2. Without act. prom.agent	143	358	161
3. Activity-promoting granule	43	112	57
4. Actipron	90	182	72
5. Armoblen T/25	31	145	82

	Dry matter (mg/seedling) Bedstraw (G.spurium)		Mayweed (M.inodorum)	
	Quinoline (Quinmerac)	Sulphonyl urea (Triasulphuron)	Pyridazine (Chloridazon)	(Pyridate)
1. Untreated	194	194	282	282
2. Without prom. agent	50	94	142	145
3. Activity-prom. granule	26	20	76	77
4. Actipron	31	22	106	22
5. Armoblen T/25	22	22	109	41

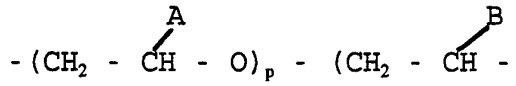
CLAIMS

1. A herbicide composition comprising at least
- one or more active ingredients, known per se, preferably benzofuran, bipyridine, hydroxybenzonitrile, carbamoyl phenyl carbamate, pyridazine, quinoline, sulphonyl urea, or triazine herbicide, and
- one or more activity-promoting agents for improving the efficacy of the active ingredient/ingredients,
c h a r a c t e r i z e d in that the activity-promoting agent is a tetraalkoxylated alkyl diamine with the following general formula (I):



(I)

in which R_1, R_2, R_3 and R_4 are groups which, independent of each other, conform to the following formula:



in which one of groups A and B is a hydrogen and the other a lower alkyl group, and p+q = 5-150, and n = 1-6, whereby the molecular weight of the compound according to formula (I) is in the range of about 1 000-40 000.

2. A herbicide composition according to Claim 1,
c h a r a c t e r i z e d in that the active ingredient is methyl-3-m-tolyl-carbamoyl oxyphenyl carbamate and/or ethyl-3-phenyl carbamoyl oxyphenyl carbamate and/or 2-ethoxy-2,3-dihydro-3,3-dimethyl benzofuran-5-ylmethane sulphonate and/or 4-amino-3-methyl-6-phenyl-1,2,4-triazine-5-(4H)-one, and/or 1,1'-ethylene-2,2'-dipyridyliumdibromide, and/or 3,5-dibromo-4-hydroxy benzonitrile and/or 5-amino-4-chlorine-2-phenylpyridazine-3-(2H)-one, and/or 6-chloro-3-phenylpyridazine-4-yl-S-octyl tiocarbonate, and/or 7-chloro-3-methyl-8-quinoline carboxylic acid, and/or 3-(6-methoxy-4-methyl-1,3,5-triazine-2-yl)-1-[2-(2-chlorethoxy)phenyl sulphonyl] urea.

3. A herbicide composition according to Claim 1 or 2, c h a r a c t e r i z e d in that it further comprises ethoxy propoxy block copolymer as a synergetic additive.

4. A herbicide composition according to Claim 3, c h a r a c t e r i z e d in that the ethoxy propoxy block copolymer conforms to the following general formula (II):

$$HO-[(CH_2-CH_2-O)_r - (CH_2-CH_3-O)_s)]_t - H \quad (II)$$

in which r and s are mainly > 5 and t has such a value that the molecular weight of the ethoxy propoxy copolymer is in the range of 2 000 - 20 000.

5. A herbicide composition according to Claim 4, c h a r a c t e r i z e d in that the ratio of the amount of ethoxy propoxy block copolymer to the amount of the tetraalkoxylated alkyl diamine is preferably 1:10 - 10:1 by weight.

6. A herbicide composition according to Claim 1, c h a r a c t e r i z e d in that the ratio of the amount of the activity-promoting agent to the amount of the active ingredient is preferably 1:5 - 10:1 by weight.

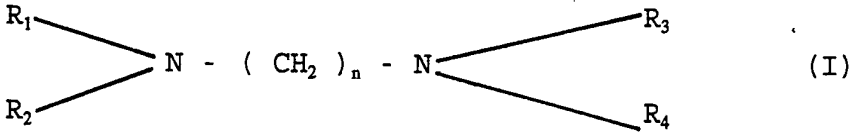
7. A herbicide composition according to Claim 1, c h a r a c t e r i z e d in that it further contains other substances such as carriers and encapsulating agents as well as additives intended for emulsification, dispersing, suspending, antifreezing, stabilizing and/or antifoaming, and/or other activity-promoting agents.

8. A herbicide composition according to Claim 2, c h a r a c t e r i z e d in that it simultaneously further comprises other pesticides such as acetamide, diphenyl ether, organophosphorus, pyridine, thiocarbamate, triazine, and uracil herbicides.

9. A method for destroying weeds, c h a r a c t e r i z e d in that weeds are treated with a herbicide composition according to

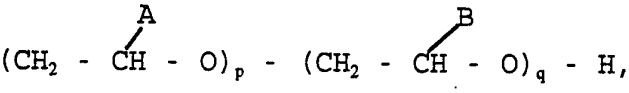
any of the preceding Claims.

10. An activity-promoting agent for improving the efficacy of the active ingredient of a herbicide, such as benzofuran, bipyridine, hydroxybenzonitrile, carbamoyl phenyl carbamate, pyridazine, quinoline, sulphonyl urea or triazine active ingredient, c h a r a c t e r i z e d in that the activity-promoting agent comprises tetraalkoxylated alkyl diamine, the general formula (I) of which is:



(I)

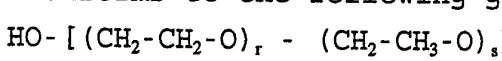
in which R_1, R_2, R_3 and R_4 are groups which, independent of each other, conform to the formula:



in which one of groups A and B is a hydrogen and the other a lower alkyl group, and p + q = 5 - 150, and n = 1 - 6, whereby the molecular weight of the composition according to formula (I) is in the range of about 1 000 - 40 000.

11. An activity-promoting agent according to Claim 10, c h a r a c t e r i z e d in that the activity-promoting agent comprises ethoxy propoxy block copolymer as a synergetic additive in addition to the tetraalkoxylated alkyl diamine.

12. An activity-promoting agent according to Claim 11, c h a r a c t e r i z e d in that the ethoxy propoxy block copolymer conforms to the following general formula (II):



(II)

in which r and s are mainly > 5 and t has such a value that the molecular weight of the ethoxy propoxy copolymer is in the range of 2 000 - 20 000.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 94/00331

A. CLASSIFICATION OF SUBJECT MATTER

IPC5: A01N 25/30
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC5: A01N

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

SE,DK,FI,NO classes as above

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

CA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chemical Abstracts, Volume 103, No 12, 23 Sept 1985 (23.09.85), (Columbus, Ohio, USA), page 86, THE ABSTRACT No 89334c, JP, A, 6075324, (Neos Co., Ltd.) 27 April 1985 (27.04.85) --	1,2,6-10
X	EP, A1, 0417896 (TAKEMOTO YUSHI KABUSHIKI KAISHA), 20 March 1991 (20.03.91) --	1-11
X	GB, A, 2233229 (RHONE-POULENC AGROCHIME), 9 January 1991 (09.01.91) --	1,2,6-10
X	EP, A1, 0257686 (AKZO N.V.), 2 March 1988 (02.03.88), claim 2, formulae III and IV --	1,2,6-10

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
21 October 1994	02 -11- 1994
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Gerd Strandell Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 94/00331

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB, A, 2022416 (KATAYAMA CHEMICAL WORKS CO LTD ET AL), 19 December 1979 (19.12.79), page 2, line 4 - line 28; the claims ---	1,2,6-10
X	EP, A2, 0302701 (ROHM AND HAAS COMPANY), 8 February 1989 (08.02.89), the claims; page 3, line 61 - page 4, line 14 --- --------	3-5,11,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/10/94

International application No.
PCT/FI 94/00331

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP-A- 6075324	27/04/85	NONE	
EP-A1- 0417896	20/03/91	JP-A- 3130202	04/06/91
GB-A- 2233229	09/01/91	AU-A- 5756590	03/01/91
		CA-A- 2019087	20/12/90
		DE-A- 4019362	03/01/91
		FR-A- 2648316	21/12/90
		JP-A- 3034901	14/02/91
		LU-A- 87747	18/02/91
		NL-A- 9001407	16/01/91
		SE-A- 9002166	21/12/90
EP-A1- 0257686	02/03/88	CA-A- 1329538	17/05/94
		US-A- 5226943	13/07/93
		ZA-A- 8706184	22/02/88
GB-A- 2022416	19/12/79	AU-B- 523906	19/08/82
		AU-A- 4555879	18/10/79
		CA-A- 1102206	02/06/81
		DE-A,C- 2913593	18/10/79
		FR-A,B- 2421620	02/11/79
		JP-C- 1184184	27/12/83
		JP-A- 54132230	15/10/79
		SE-B,C- 446809	13/10/86
		SE-A- 7902934	06/10/79
		US-A- 4206886	10/06/80
		US-A- 4289581	15/09/81
		US-A- 4334957	15/06/82
		JP-C- 1184185	27/12/83
		JP-A- 54135223	20/10/79
EP-A2- 0302701	08/02/89	SE-T3- 0302701	
		AU-A- 2040488	20/04/89
		CA-A- 1297402	17/03/92
		DE-D,T- 3886127	28/04/94
		FI-C- 90816	11/04/94
		JP-A- 1131102	24/05/89
		US-A- 4954338	04/09/90