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(54) Title: GLYPHOSATE COMPOSITIONS AND THEIR USE

(57) Abstract: The invention relates to a herbicidal composition comprising: (a) glyphosate acid or an agriculturally acceptable salt or derivative thereof, and (b) a surface active component having formula (i) or a quaternized form thereof or the amine oxide derivative thereof, wherein R1 and R2 each independently represent a straight or branched chain alkyl or alkenyl group having from 4 to 24 C-atoms, R_3 in each (R_3-O)-group may be the same or different and represents alkylene having from 2 to 4 carbon atoms, and x and y are average numbers such that x+y is in the range from 2 to 160. It further relates to adjuvant compositions comprising such surface active compounds and to a method for the control compositions. These compositions show improved herbicidal efficacy and may contain high concentrations of glyphosate.

GLYPHOSATE COMPOSITIONS AND THEIR USE

The present invention relates to improved herbicidal glyphosate compositions comprising a glyphosate herbicide and surfactants.

Glyphosate is a well known highly effective and commercially important non-selective systemic herbicide for combating a wide variety of unwanted vegetation, including agricultural weeds. Glyphosate is conventionally applied as a formulated product comprising the active ingredient and a surface active component, dissolved in water, to the foliage of the plants.

Usually, glyphosate is formulated in commercial compositions in the form of a water-soluble salt. Salts in commercial use include the ammonium salt, alkylamine salts, such as the isopropylamine salt, alkali metal salts, such as the sodium salt, and the trimethylsulfonium salt.

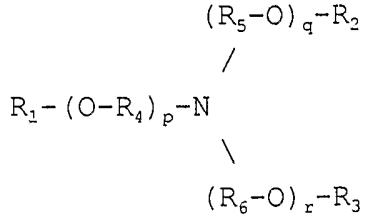
Numerous studies have been made on the effect of surfactants or surfactant combinations on the herbicidal action of glyphosate. Wyrill and Burnside, Weed Science, Vol. 25 (1977), 275-287, studied the effects of many different surfactants including examples from different classes of surfactant. Some classes of surfactant were more effective than others in enhancing the herbicidal effect of glyphosate (used as a solution of the isopropylamine salt). Wyrill and Burnside concluded that an effective surfactant is an important component of any glyphosate spray formulation.

Monsanto's well known commercial liquid formulation sold for years under the tradename Roundup® comprises, per liter of formulated product, 360 g a.e.

(acid equivalent) of glyphosate in the form of its isopropylamine salt and 180 g of a tallow amine ethoxylate surfactant.

Efforts have been made in recent years to develop glyphosate compositions that show improved efficacy in general or in certain conditions, and/or which show improved environmental profiles. There also have been developed advantageous solid compositions.

WO95/33379 discloses trialkanolamine derivatives and quaternized derivatives thereof for enhancement of the efficacy of agricultural chemicals. It more particularly discloses compounds of the formula



wherein R1 represents *inter alia* a linear or branched alkyl group or alkenyl group having 5 to 29 carbon atoms, R_2 and R_3 may be the same or different and each represent hydrogen or a linear or branched alkyl or alkenyl group having from 5 to 29 carbon atoms, p, q, and r may be the same or different and each represent a number of 1 to 30 in the average, and R_4, R_5 and R_6 represent alkylene groups of 2 to 4 carbon atoms, for use with agricultural chemicals. Herbicidal compositions comprising glyphosate are also disclosed. Example 1, Table 9 suggests herbicidal compositions comprising Roundup® herbicide and a compound of the above formula wherein R_1 and R_2 are alkyl with 18 C-atoms, R_3 is hydrogen, and p, q and r are each 5.

More recently, WO96/32839 discloses herbicidal glyphosate compositions comprising an effective herbicidal activity enhancing amount of a surfactant having the

chemical formula

$$R_1-(O-R_2)_m-N\begin{matrix}(R_3-O)_x-H\\ \\ (R_3-O)_y-H\end{matrix}$$

wherein x and y are average numbers such that x+y is in the range from 2 to 60; or

$$R_1-(O-R_2)_m-N^+-R_4\ \ A^-\begin{matrix}(R_3-O)_x-H\\ \\ (R_3-O)_y-H\end{matrix}$$

wherein x+y is in the range from 0 to 60, and A- is an agriculturally acceptable anion, R_4 is C_1-C_4 alkyl; or

$$R_1-(O-R_2)_m-N\rightarrow O\begin{matrix}(R_3-O)_x-H\\ \\ (R_3-O)_y-H\end{matrix}$$

wherein x+y is in the range from 2 to 60,
and where in all the above formulae, R_1 is a straight or branched chain alkyl, aryl, or alkylaryl group having from 6 to 22 carbon atoms, m is an average number from 1 to 10, R_2 and R_3 in each of the m $(O-R_2)$ or (R_3-O) groups is independently alkylene with 1 to 4 carbon atoms. Such compositions may show very high glyphosate concentrations ranging from 450 to 500 g a.e./l while still showing an adequate surfactant concentration. Such compositions are said to show excellent herbicidal performance and a good storage stability under a wide range of temperatures.

An aim of the present invention is to provide improved herbicidal glyphosate compositions.

Another aim of the present invention consists

in providing new glyphosate formulations which show an advantageous herbicidal activity together with an acceptable environmental profile.

According to the present invention herbicidal compositions comprise

(a) glyphosate acid or an agriculturally acceptable salt or derivative thereof, and

(b) a surface active component having the formula

$$\begin{array}{l} (R_3\text{-}O)_x\text{-}R_1 \\ / \\ R\text{-}N \\ \backslash \\ (R_3\text{-}O)_y\text{-}R_2 \end{array} \qquad (I)$$

or a quaternized form thereof

$$\begin{array}{l} (R_3\text{-}O)_x\text{-}R_1 \\ / \\ RR'\text{-}N^+ \qquad A^- \\ \backslash \\ (R_3\text{-}O)_y\text{-}R_2 \end{array} \qquad (II)$$

or the amine oxide derivative thereof

$$\begin{array}{l} (R_3\text{-}O)_x\text{-}R_1 \\ / \\ R\text{-}N\text{->}O \\ \backslash \\ (R_3\text{-}O)_y\text{-}R_2 \end{array} \qquad (III)$$

wherein R and R′ represent hydrogen or alkyl having 1 to 3 carbon atoms, R1 and R2 each independently represent a straight or branched chain alkyl or alkenyl group having from 4 to 24 C-atoms, R_3 in each $(R_3\text{-}O)$-group may be the same or different and represents alkylene having from 2 to 4 carbon atoms, A^- is an agriculturally acceptable anion, and x and y are average numbers such that x+y is in the range from 2 to 160.

Such compositions show a surprisingly high

degree of herbicidal efficacy compared to prior art compositions, in the sense that, at typical glyphosate/surfactant ratios, the efficacy is at least similar to, but at increased glyphosate/surfactant ratios is drastically improved over, conventional surfactant(s) containing compositions. Invention compositions show similar performance or biological effect to prior art compositions, with the advantage of using higher glyphosate/surfactant ratios. As a result, compositions of the invention may contain higher concentrations of glyphosate and be economically more interesting.

As used herein, "glyphosate" means N-phosphonomethylglycine in its acid form as well as in any salt form or derivative of glyphosate which in aqueous solution provides glyphosate anions along with suitable cation. Glyphosate includes the isopropylamine salt of glyphosate and other agriculturally acceptable salts of glyphosate such as those disclosed in US Patent 3,799,758.

Surfactants as defined hereabove are known to the person skilled in the art and may be prepared by ammonolysis of the corresponding alcohol (alkoxylated or not) with ammonia and a suitable catalyst. According to that method of preparation, the relevant alcohol or an alcohol mixture is heated in the presence of a suitable catalyst, such as for example a nickel catalyst, to a temperature ranging from 130 to 220 degrees C, preferably to about 190 degrees C, while flushing with nitrogen. Ammonia and hydrogen are then added continuously at a proportion of 5 to 1 to 1 to 2 by volume, preferably around 3 to 1. The pressure of the reaction medium can be varied from normal pressure to medium pressure conditions of approximately 20 bar. The resultant surfactant is obtained after 9 to 20 hours, after distillation of the reaction water. After the reaction is completed, the

product is cooled to room temperature, the catalyst is filtered off and the product is degassed in an evaporator. The product obtained may the further be reacted according to standard procedures in view of desirable alkoxylation, methylation, oxidation or quaternization.

In the compositions of the invention, the weight ratio of glyphosate (expressed as glyphosate acid equivalent) to the total surface active component can vary over a considerable range, for example from 1:5 to 20:1. The optimum ratio will vary according to the manner and conditions in which the herbicidal composition is applied, the weed species to be treated, and the particular surfactant used, but is normally higher than 1:1, preferably higher than 2:1, more particularly higher than 5:1. Compositions of the invention are so advantageously effective that compositions with unexpectedly high glyphosate a.e./surfactant ratios of the order of 20:1 or 15:1 still give good results. Compositions having a glyphosate a.e. to surfactant ratio of 8:1, 10:1 or 12:1 are particularly preferred. Such compositions show an acceptable commercial control of undesired plants similar to current commercial and prior art compositions while containing a reduced surfactant level.

A composition of the invention can be a liquid concentrate intended to be diluted with water to form a spray solution for the herbicidal application. A liquid concentrate will normally contain at least 50 grams glyphosate acid equivalent per litre, and preferably at least 200 g/l, up to 600 g/l but in certain cases, more diluted ready to use formulations may contain glyphosate concentrations of about 2 to 20 g/l. Compositions containing 300 to 600 g/l or 400 to 550 g/l are preferred.

In another form, a composition of the invention

is a solid, for example a free-flowing particulate, granular solid or compressed into tablets or briquettes of any desired size and shape. Such compositions will usually contain not more than 5% and preferably not more than 1% by weight of water. Solid compositions may be formulated to include a water-soluble inert carrier, and for this purpose ammonium salts such as ammonium sulphate may be particularly suitable (see below). The weight ratio of glyphosate (expressed as glyphosate acid equivalent) to surface active component in such compositions will be within the general range mentioned above. The amount of water-soluble inert carrier is not critical, and in the case of ammonium sulphate, the amount may, for example, range from 0% to 80% of the total weight of the composition. A dry composition normally contains at least 5 - 80 % w/w glyphosate acid equivalent. Solid compositions can be made, for example by spray drying an aqueous solution of the components, by dry-blending the ingredients in conventional granulating apparatus, or by extrusion blending whereby a granular product is obtained in an essentially single operation.

Compositions of the invention also include spray solutions. In these solutions, the concentration of glyphosate is selected according to the volume per unit area of spray solution to be used and the desired rate of application of glyphosate per unit area. For example, conventional spraying is done at 50-800 litres of spray solution per hectare, and the rate of application of glyphosate is typically 0.125 to 4 kg of glyphosate acid equivalent per hectare. In controlled drop spraying, the rate of application of glyphosate per hectare will normally be within the same range, but the volume of spray solution per hectare will be considerably less, perhaps 15-50 litres per hectare. Spray solutions for controlled drop spraying are therefore more concentrated than those

used in conventional spraying.

Spray solution compositions can be prepared by diluting liquid concentrates or dissolving solid compositions of this invention as described above, or by tank mixing the separate components of the claimed compositions.

Compositions of the invention may include a significant amount of an agriculturally-acceptable inorganic ammonium salt such as ammonium nitrate, ammonium thiocyanate, ammonium thiosulfate, ammonium phosphate, ammonium chloride, preferably ammonium sulphate, in addition to the glyphosate herbicide and surface active component.

Compositions of the invention, more particularly formulated concentrate compositions of the invention may further contain other adjuvants like formulation aids, such as extrusion aids, dyes, thickeners, defoamers, such as silicon based defoamers, stabilizers, anti-freeze agents such as ethylene glycol and other surfactants, or even other pesticidal actives, as may be determined by the person skilled in the art.

Preferably R1 and R2 each independently represent a straight or branched chain alkyl or alkenyl group having from 8 to 18 carbon atoms.

Surfactants corresponding to formula (I) are preferred. Most preferred are surfactants of formula (I) wherein R1 and R2 each independently are a straight or branched chain alkyl or alkenyl group having 12 to 18 carbon atoms.

x+y may range from 2 to 160 or even more while

maintaining the good efficacy of the surfactant in the invention compositions. An advantageous alkoxylation degree ranges from x+y = 4 to 100, preferably 6 to 50. In certain instances, depending on the actual chemical structure of the surfactant, an alkoxylation degree of x+y comprised between 8 and 20, or 10 to 20 or preferably 12 to 20 has shown particularly advantageous.

Another embodiment pertaining to the present invention includes an adjuvant for agricultural compositions, more particularly herbicidal glyphosate compositions, which comprises a surface active component as per formulae (I) to (III).

Adjuvant compositions of the invention, similarly to the herbicidal compositions of the invention as described above can optionally contain other components.

The concentrates and solutions of the invention may also be mixed with other pesticides. Preferably though not required such other herbicides, insecticides or fungicides have low irritancy and toxicity.

Yet another aspect of the present invention is a method of use of compositions described above for the control of unwanted vegetation.

The invention will be described in more detail hereafter with reference to examples.

EXAMPLE 1

A solid composition (cmps 1) according to the invention was prepared as follows:

Ammonium salt of glyphosate (MON8750 powder), surfactant of formula $C_{12-18}H_{25-37}-(OCH_2CH_2)_5-NH-(CH_2CH_2O)_5-C_{12-18}H_{25-37}$ (surfactant 1) and Rhodorsil 432 (tradename) antifoam were blended in that order at room temperature in a Hobart planetary mixer. Water was then added and mixing continued until a dough is formed with a consistency suitable for extrusion. The dough mixture was charged into a Fuji Paudal EXDS-60 extruder fitted with a 0.7 mm radial screen. The extruded granules were dried using an Aeromatic Strea-1 fluid bed dryer controlled at approx 50 degrees C for approx 30 minutes, and sieved on an Endecotts EFL MK3 sieve shaker. Fines of <0.3mm and oversize >2.0mm in size were removed by the sieving process and discarded. The final product was comprised of free flowing, non-dusty off white coloured granules.

Final composition was as follows:

ammonium glyphosate (MON8750 powder)	89.81 %w/w
surfactant N. 1	9.70
Rhodorsil 432	0.49

The product had an initial residual moisture content of < 1 % w/w.

Details of storage stability test results can be seen in the table below. Assay of the formulation indicated no loss of glyphosate active ingredient after one month at 54 degrees C compared to a sample stored at -18 degrees C for the same period. The formulation was found not to foam on dilution when tested according to method CIPAC MT47.2 at a concentration of 6.4g product in 230ml of water. The dissolution and solution stability was tested according to CIPAC method MT179 at a concentration of 6.9g of formulation in 250ml of water; both initially and after storage for two weeks at 54 degrees C the formulation was

found to dissolve within the specified 5 minutes and the solution thus formed exhibited no precipitation or phase separation after 18 hours.

		Initial	2 weeks @ 54C	1 month @ 54C
Assay (%w/w glyphosate acid equivelant)		77.3	80.0	77.6
Persistent foaming (ml after 1 minute)		0	0	0
Dissolution & solution stability	5 mins	Pass	Pass	Insufficient sample
	18 hours	Pass	Pass	Insufficient sample
pH (1% w/v)		3.7	3.7	3.7

EXAMPLE 2

The herbicidal efficacy of the composition of Example 1 was evaluated in a greenhouse test, in comparison with prior art compositions:

- cmps a, commercial Roundup® comprising 360 g/l glyphosate a.e. and 180 g/l tallow amine ethoxylate (15 EO) based surfactant;
- cmps b, commercial glyphosate composition sold under the tradename Roundup® Bioforce® in France, comprising 360 g/l glyphosate a.e. and 180 g/l of a surfactant composition comprising a propoxylated quaternary ammonium surfactant as per Example 6 of EP-0 441 764;
- cmps c, a soluble liquid comprising 81.80% w/w isopropylamine salt of glyphosate (grade 205 - 46 %w/w of glyphosate acid equivalent) and 7.53 %w/w surfactant as per WO96/32839 (having the amine structure wherein R1 is a branched alkyl chain having 11 - 14 C-atoms, R2 is isopropyl, m is 1, R3 is ethylene oxide and x+y is 5.

The rates of application of this test were equivalent to 240, 480, 720 and 960 g a.e./ha.

Agropyron repens (AGRRE - narrow leaf) and Raphanus sativus (RAPSA - broadleaf) plants were grown from seed in 10 cm pots containing a natural sandy loam soil. The pots were placed in a growth-room until the spraying with a precise relative humidity as well as temperature control. After spraying plants were transferred to a greenhouse where light and temperature were also well controlled. Plants remained in this greenhouse for the remainder of the experiment. Both in growth-room and in the greenhouse, the water was supplied from below the pots by an automatic irrigation system.

Plants reached the appropriate growth stage for spraying around 3-4 weeks after sowing. Before spraying, pots were selected for uniformity as far as possible and atypical pots were discarded.

Glyphosate compositions were applied post-emergence with a precision laboratory sprayer (IMAG-DMLO), delivering a volume of 200 l/ha solution through "Flat Even" nozzles (11003) in a single pass. All compositions were diluted in water. All replicate pots (4 pots per treatment) were sprayed with one pass of the sprayer.

Pots were distributed randomly in the growth room after treatment. Untreated control pots were placed at random among treated pots.

Assessment of per cent phytotoxicity was made by comparison with untreated control pots on an arbitrary scale from 0 to 100%, where 0 means no visible effect and 100 means death of all plants.

The results are presented as average values of four replicates and three assessments at 24 days after treatment.

TABLE 1A: Efficacy on RAPSA

Rate (g a.e./ha)	240	480	720	960
Composition a	55	89	75	85
b	53	70	80	81
c	63	73	81	89
1	65	83	92	87

TABLE 1B: Efficacy on AGRRE

Rate (g a.e./ha)	240	480	720	960
Composition a	25	69	85	92
b	23	54	84	91
c	28	73	91	97
1	26	64	85	91

As can easily be seen from the above, all compositions provide similar performance, with no significant statistical difference between them, although the invention composition comprises far less surfactant than the prior art compositions.

EXAMPLE 3

In this Example, the following surfactants were used:

R_1=R_2=	(R_3-O)=EO x+y=	R	surfactant N.
sat., branched C13 (isotridecyl)	16	H	2
	30	H	3
sat., linear C16/18 (tallow)	16	H	5
	16	CH3	6
	40	H	8
unsat., linear, C16/18 (oleyl)	16	H	9
	40	H	10
sat., C24 (guerbet)	40	H	11

Surfactant N.4 corresponds to the formula $RN[(EO)_{x'}(PO)_{x''}R_1]_2$ wherein x'=3 and x"=3, R is H and R_1 is isotridecyl.

Surfactant N.7 corresponds to a quaternized compound according to formula (II) wherein R is CH_3, R' is CH_3, R_3 is ethylene, x + y is 16, and R_1 is a saturated, linear alkyl chain from tallow.

The tested compositions were tank mixed compositions comprising isopropylamine salt of glyphosate and the relevant surfactant in a ratio of 5:1.

Glyphosate was applied at dose rates of 360, 720 and 1080 g a.e./ha following essentially the procedure as detailed in Example 2. Plant species tested were Elymus repens (narrowleaf), Raphanus sativus (broadleaf), Ipomea purpurea (broadleaf). Phytotoxicity was evaluated and recorded at 6, 18, and 25 days after treatment (DAT).

The results are presented as average values of four replicates at the dose rates and DAT as indicated.

Table III

Glypho-sate rate	RAPSA 6 DAT	AGRRE 6 DAT	IPOPU 6 DAT	RAPSA 15 DAT	AGRRE 18 DAT	IPOPU 18 DAT
IPA-G sur 1						
360	18.8	10.0	32.5	60.0	76.3	57.5
720	23.8	20.0	47.5	70.0	90.0	85.0
1080	25.0	20.0	36.3	61.3	93.8	75.0
IPA-G sur 2						
360	17.5	18.8	27.5	42.5	76.3	52.5
720	22.5	23.8	31.7	60.0	82.5	80.0
1080	27.5	26.3	53.8	72.5	94.0	88.8
IPA-G sur 3						
360	17.5	15.0	30.0	43.8	65.0	60.0
720	27.5	25.0	46.7	63.8	91.5	90.0
1080	27.5	20.0	51.3	67.5	91.3	90.0
IPA-G sur 4						
360	16.3	26.3	20.0	40.0	90.3	61.3
720	20.0	25.0	26.3	52.5	91.5	72.5
1080	21.3	27.5	31.3	56.3	94.5	85.0

TABLE III con't

Glypho-sate rate	RAPSA 6 DAT	AGRRE 6 DAT	IPOPU 6 DAT	RAPSA 15 DAT	AGRRE 18 DAT	IPOPU 18 DAT
IPA-G sur 5						
360	25.0	20.0	30.0	51.7	73.8	71.3
720	21.3	21.3	27.5	68.8	85.0	78.8
1080	21.3	37.5	50.0	76.3	97.3	91.3
IPA-G sur 6						
360	17.5	17.5	36.3	47.5	70.0	61.3
720	20.0	32.5	47.5	61.3	92.8	86.3
1080	21.3	22.5	41.3	58.8	92.0	91.3
IPA-G sur 7						
360	16.3	10.0	20.0	43.8	58.8	58.8
720	20.0	12.5	35.0	61.3	72.5	87.5
1080	22.5	32.5	35.0	65.0	93.3	90.0
IPA-G sur 8						
360	16.3	13.8	40.0	46.3	75.0	77.5
720	18.8	12.5	40.0	51.3	80.0	81.3
1080	26.3	13.8	41.3	81.3	86.3	92.5
IPA-G sur 9						
360	18.8	17.5	31.3	48.8	77.5	72.5
720	23.8	17.5	37.5	57.5	83.8	85.8
1080	27.5	21.3	36.3	77.5	90.8	92.5

TABLE III con't

Glypho-sate rate	RAPSA 6 DAT	AGRRE 6 DAT	IPOPU 6 DAT	RAPSA 15 DAT	AGRRE 18 DAT	IPOPU 18 DAT
IPA-G sur 10						
360	17.5	13.8	35.0	51.3	77.5	77.5
720	20.0	25.0	42.5	67.5	92.8	92.0
1080	21.3	22.5	45.0	60.0	92.0	93.8
IPA-G sur 11						
360	17.5	10.0	33.8	58.8	65.0	72.5
720	28.8	17.5	33.8	72.5	91.3	85.0
1080	27.5	17.5	35.0	71.3	91.3	83.8
IPA-G sur 1						
360	70.0	86.3	56.7			
720	77.5	97.8	93.3			
1080	75.0	100.0	87.5			
IPA-G sur 2						
360	55.0	82.5	60.0			
720	80.0	93.8	87.7			
1080	84.5	99.5	97.0			

TABLE III con't

Glypho-sate rate	RAPSA 25 DAT	AGRRE 25 DAT	IPOPU 25 DAT
IPA-G sur 3			
360	55.0	75.0	70.0
720	76.3	98.0	98.3
1080	81.3	98.8	96.5
IPA-G sur 4			
360	52.5	93.3	72.5
720	63.8	95.8	83.8
1080	72.5	99.5	90.8
IPA-G sur 5			
360	60.0	80.0	77.0
720	86.3	97.0	87.0
1080	87.5	99.0	97.0
IPA-G sur 6			
360	60.0	75.0	73.8
720	75.0	96.5	95.8
1080	89.5	98.3	97.3
IPA-G sur 7			
360	61.3	71.3	68.8
720	78.8	82.5	95.8
1080	81.3	98.3	97.3

TABLE III con't

Glypho-sate rate	RAPSA 25 DAT	AGRRE 25 DAT	IPOPU 25 DAT
IPA-G sur 8			
360	61.3	83.3	83.8
720	70.0	93.8	92.0
1080	91.3	97.0	96.5
IPA-G sur 9			
360	62.5	83.8	76.3
720	72.5	93.3	96.5
1080	93.3	98.8	96.5
IPA-G sur 10			
360	60.0	81.3	86.3
720	85.0	98.3	95.8
1080	78.8	99.5	95.0
IPA-G sur 11			
360	75.0	70.0	81.3
720	86.5	97.8	94.5
1080	90.8	98.5	92.0

IPA-G: means isopropyl amine salt of glyphosate;
sur: means surfactant followed by the number of the surfactant as referred to earlier;
360, 720 and 1080 mean grams acid equivalent per hectare.

This Example shows that, at glyphosate a.e./surfactant

ratios of 5/1, all these invention compositions perform very well and to a similar extent.

EXAMPLE 4

A similar test was performed according to essentially the same protocol, except that evaluations were made as indicated (DAT).

Compositions tested were as follows:

- composition a, as defined in Example 2;
- composition b, as defined in Example 2;
- composition c, as defined in Example 2;
- a tank mix comprising a 10/1 ratio of glyphosate isopropylamine salt and surfactant 1;
- a tank mix comprising a 10/1 ratio of glyphosate isopropylamine salt and surfactant 3;
- a tank mix comprising a 10/1 ratio of glyphosate isopropylamine salt and surfactant 4;
- a tank mix comprising a 10/1 ratio of glyphosate isopropylamine salt and surfactant 5;
- a tank mix comprising a 10/1 ratio of glyphosate isopropylamine salt and surfactant 9;
- a tank mix comprising a 10/1 ratio of glyphosate isopropylamine salt and surfactant 11.
- a tank mix composition comprising isopropylamine salt of glyphosate and surfactant N. 12 (R1=R2= C24 guerbet, (R3-O) is EO, x+y=160, and R=H) in a ratio of 10:1;

The test results are summarized in Table IV below.

TABLE IV

Glypho-sate rate	RAPSA 11 DAT	IPOPU 11 DAT	AGRRE 18 DAT	RAPSA 26 DAT	AGRRE 26 DAT	IPOPU 27 DAT
cps a						
360	35.0	21.3	37.5	65.0	52.5	38.8
720	56.3	41.3	60.0	82.5	73.8	63.8
1080	62.5	38.8	75.0	85.0	80.0	67.5
cps b						
360	28.8	30.0	41.3	52.5	51.3	50.0
720	37.5	17.5	71.3	70.0	77.5	57.5
1080	43.8	55.0	85.0	76.3	83.8	73.8
cps c						
360	27.5	13.8	42.5	42.5	50.0	35.0
720	43.8	37.5	72.5	73.8	81.3	53.8
1080	52.5	40.0	82.5	82.5	86.3	73.8
IPA-G sur 12						
360	41.3	16.3	31.3	63.8	37.5	41.3
720	45.0	51.3	45.0	83.8	53.8	61.3
1080	56.3	33.8	53.8	80.0	70.0	65.0
IPA-G sur 1						
360	33.8	17.5	36.3	58.8	42.5	38.8
720	48.8	35.0	52.5	72.5	71.3	60.0
1080	50.0	55.0	73.8	78.8	83.8	68.8

Glypho-sate rate	RAPSA 11 DAT	IPOPU 11 DAT	AGRRE 18 DAT	RAPSA 26 DAT	AGRRE 26 DAT	IPOPU 27 DAT
IPA-G sur 3						
360	33.8	25.0	30.0	53.8	53.0	41.3
720	46.3	36.3	46.3	72.5	61.3	57.5
1080	55.0	42.5	68.8	82.5	78.8	65.0
IPA-G sur 4						
360	30.0	17.5	30.0	43.8	31.3	31.3
720	40.0	27.5	38.8	65.0	50.0	40.0
1080	50.0	41.3	60.0	78.8	71.3	58.8
IPA-G sur 5						
360	37.5	16.3	31.3	65.0	33.8	30.0
720	47.5	25.0	48.8	76.3	62.5	41.3
1080	55.0	38.8	42.5	85.0	56.3	62.5
IPA-G sur 9						
360	37.5	37.5	33.8	66.3	46.3	56.3
720	43.8	36.3	48.8	72.5	58.8	67.5
1080	61.3	48.8	76.3	83.8	82.5	73.8
IPA-G sur 11						
360	46.3	17.5	35.0	73.8	45.0	33.8
720	50.0	20.0	48.8	81.3	62.5	45.0
1080	45.0	33.8	48.8	76.3	62.5	58.8

IPA-G means isopropylamine salt of glyphosate;
sur means surfactant followed by the surfactant number

which refers to the corresponding surfactant definition; 360, 720 and 1080 are the glyphosate acid equivalent dose rates applied, expressed in grams/ha.

This example shows that at glyphosate a.e./surfactant ratios as high as 10:1 the compositions of the invention perform unexpectedly well, and as good as prior art compositions with ratios of 5:1 or 2:1.

EXAMPLE 5

A similar test was performed according to essentially the same protocol.

The tested compositions were prior art compositions a, b and c, and tank mixed compositions comprising isopropylamine salt of glyphosate and the relevant surfactant in a ratio of 5:1.

The surfactants used in this test are as follows:

$R_1=R_2=$	$(R_3-O)=EO$ x+y=	R	surfactant N.
sat., linear C8/10	16	H	13
	20	H	14
sat., linear C12/18	20	H	15
	16	H	16
sat., linear C8/10	10	H	17

Glyphosate was applied at dose rates of 360, 720 and 1080 g a.e./ha following essentially the procedure as detailed in Example 2. Plant species tested

were Elymus repens (narrowleaf), Raphanus sativus (broadleaf), Ipomea purpurea (broadleaf). Phytotoxicity was evaluated and recorded at 6, 17, and 25 days after treatment (DAT).

The results are presented as average values of four replicates at the dose rates and DAT as indicated on each Table.

Table V

Glypho-sate rate	RAPSA 6 DAT	AGRRE 6 DAT	IPOPU 6 DAT	RAPSA 17 DAT	AGRRE 17 DAT	IPOPU 17 DAT
cps a						
360	55.0	16.3	20.0	83.3	61.3	42.5
720	63.8	43.8	23.8	90.8	86.3	63.8
1080	72.5	47.5	31.3	95.8	96.3	79.5
cps b						
360	43.3	16.3	25.0	65.0	55.0	60.0
720	50.0	50.0	27.5	87.5	95.3	70.0
1080	55.0	58.8	37.5	92.0	97.5	72.5
cps c						
360	36.7	35.0	20.0	78.3	61.3	48.8
720	58.8	53.8	27.5	91.3	95.8	65.0
1080	66.3	43.8	30.0	95.0	93.8	84.5
IPA-G sur 1						
360	28.3	23.8	20.0	61.7	61.3	51.3
720	62.5	31.3	30.0	88.3	87.5	73.8
1080	76.3	32.5	26.3	99.5	99.5	73.8

TABLE V con't

Glyphosate rate	RAPSA 6 DAT	AGRRE 6 DAT	IPOPU 6 DAT	RAPSA 17 DAT	AGRRE 17 DAT	IPOPU 17 DAT
IPA-G sur 13						
360	45.0	27.5	15.0	77.7	81.3	37.5
720	56.3	40.0	33.8	87.5	98.8	68.8
1080	56.3	41.3	35.0	88.3	99.5	78.8
IPA-G sur 14						
360	48.3	17.5	26.3	76.0	63.8	41.3
720	68.3	30.0	28.8	97.5	94.5	52.5
1080	62.5	46.3	31.3	86.3	97.5	68.8
IPA-G sur 15						
360	40.0	16.3	22.5	61.7	48.8	45.0
720	55.0	26.3	33.8	92.0	90.8	70.0
1080	65.0	21.3	35.0	94.5	95.8	78.8
IPA-G sur 16						
360	45.0	15.0	22.5	75.0	43.8	47.5
720	55.0	27.5	22.5	96.3	87.5	50.0
1080	77.5	25.0	33.8	100.0	93.8	73.8
IPA-G sur 17						
360	35.0	15.0	21.3	60.0	65.0	42.5
720	63.8	20.0	31.3	87.5	81.3	57.5
1080	70.0	18.8	37.5	93.3	93.8	71.3

TABLE V con't

Glypho-sate rate	RAPSA 25 DAT	AGRRE 25 DAT	IPOPU 25 DAT
cps a			
360	89.3	67.5	51.3
720	95.0	92.5	67.5
1080	96.3	98.5	83.3
cps b			
360	68.3	61.3	65.0
720	93.3	98.8	76.3
1080	97.5	99.0	80.0
cps c			
360	76.7	71.3	57.5
720	93.8	98.5	72.5
1080	97.5	96.3	93.8
IPA-G sur 1			
360	68.3	68.8	61.3
720	91.3	96.0	82.5
1080	100.0	100.0	82.5
IPA-G sur 13			
360	83.3	89.5	46.3
720	93.8	99.5	75.0
1080	95.8	100.0	90.0

TABLE V con't

Glypho-sate rate	RAPSA 25 DAT	AGRRE 25 DAT	IPOPU 25 DAT
IPA-G sur 14			
360	81.7	70.0	56.3
720	98.8	97.8	61.3
1080	92.0	99.5	78.8
IPA-G sur 15			
360	68.0	57.5	56.3
720	93.8	95.3	76.3
1080	96.3	99.0	85.8
IPA-G sur 16			
360	76.7	51.3	61.3
720	98.3	90.0	63.8
1080	100.0	99.0	80.0
IPA-G sur 17			
360	61.7	70.0	58.8
720	91.3	87.5	63.8
1080	95.0	97.8	79.0

IPA-G means isopropylamine salt of glyphosate;
sur means surfactant followed by the surfactant number which refers to the corresponding surfactant definition;
360, 720 and 1080 are the glyphosate acid equivalent dose rates applied, expressed in grams/ha.

This example shows that at glyphosate a.e./surfactant

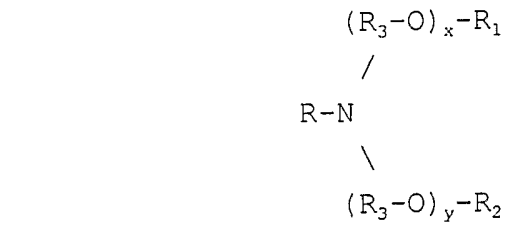
ratios of 5:1 the compositions of the invention perform unexpectedly well compared to prior art compositions with ratios of 5:1 or 2:1.

CLAIMS

1. Herbicidal composition comprising:

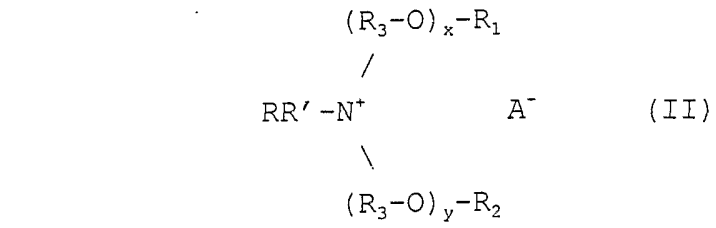
(a) glyphosate acid or an agriculturally acceptable salt or derivative thereof, and

(b) a surface active component having the formula



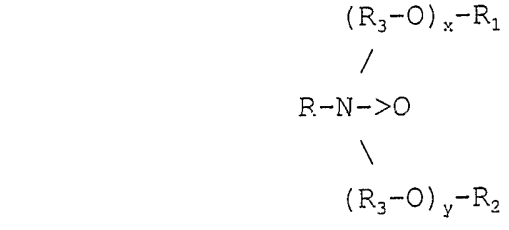
(I)

or a quaternized form thereof



(II)

or the amine oxide derivative thereof



(III)

wherein R and R′ represent hydrogen or alkyl having 1 to 3 carbon atoms, R1 and R2 each independently represent a straight or branched chain alkyl or alkenyl group having from 4 to 24 C-atoms, R_3 in each (R_3-O)-group may be the same or different and represents alkylene having from 2 to 4 carbon atoms, A^- is an agriculturally acceptable anion, and x and y are average numbers such that x+y is in the range from 2 to 160.

2. Composition according to Claim 1 wherein R1 and R2 represent a straight or branched chain alkyl or alkenyl group having from 8 to 18 C-atoms.

3. Composition according to Claim 1 or 2 wherein the surfactant is a surfactant according to formula (I).

4. Composition according to Claim 3 where in the surfactant formula R1 and R2 each independently represent a straight or branched chain alkyl or alkenyl group having from 12 to 18 C-atoms.

5. Composition according to any preceding Claim where in the surfactant formula x+y ranges from 4 to 100, preferably from 6 to 50.

6. Composition according to any preceding Claim where the weight ratio of glyphosate (expressed as glyphosate acid equivalent) to the total surface active component ranges from 1:5 to 20:1.

7. Composition according to Claim 6 wherein the weight ratio of glyphosate (expressed as glyphosate acid equivalent) to the total surface active component is higher than 1:1, preferably higher than 2:1, more particularly higher than 5:1.

8. Composition according to Claim 7 wherein the glyphosate a.e./surfactant ratio is as high as 15:1.

9. Composition according to any of claims 6 to 8 wherein the weight ratio of glyphosate (expressed as glyphosate acid equivalent) to the total surface active component is about 8:1, 10:1 or 12:1.

10. Adjuvant composition comprising a surfactant as defined in any of Claims 1 to 5, possibly together with other adjuvants, like solvent or diluent such as water or a lower alcohol, such as isopropanol or glycol, inorganic ammonium salt, dyes, thickeners, stabilizers and/or other

MISSING AT THE TIME OF PUBLICATION

INTERNATIONAL SEARCH REPORT

Inte al Application No
PCT/EP 01/05022

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 A01N57/20 //(A01N57/20,25:30)

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)
IPC 7 A01N

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

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

WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 17358 A (MONSANTO CO ;BECHER DAVID Z (US); FORBES JAMES C (US); WIDEMAN AL) 15 March 2001 (2001-03-15) page 1, line 3 - line 6 page 6, line 26 -page 7, line 2 page 7, line 20 - line 24 ---	1,2,5-9
X	WO 01 05225 A (MONSANTO CO) 25 January 2001 (2001-01-25) page 2, line 6 - line 30 page 4, line 11 - line 13 page 4, line 25 - line 26 page 6, line 11 - line 14 page 7, line 8 - line 17 page 8, line 7 - line 17 ---	1,3,5-9

-/--

[X] Further 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 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
5 February 2002	12/02/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Lamers, W

INTERNATIONAL SEARCH REPORT

Int al Application No
PCT/EP 01/05022

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 01/05022

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 10 and higher

Page 31 of the present application is missing. Therefor claims from number 10 on could not be searched.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int ial Application No
PCT/EP 01/05022

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INTERNATIONAL SEARCH REPORT

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Int nal Application No
PCT/EP 01/05022

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