

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
6 January 2011 (06.01.2011)

PCT

(10) International Publication Number
WO 2011/000880 A2

(51) International Patent Classification:

A01N 25/30 (2006.01) A01P 13/00 (2006.01)
A01N 57/20 (2006.01) A01N 25/22 (2006.01)

(21) International Application Number:

PCT/EP2010/059304

(22) International Filing Date:

30 June 2010 (30.06.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

VA2009A000040 1 July 2009 (01.07.2009) IT

(71) Applicant (for all designated States except US): LAMBERTI SPA [IT/IT]; Ufficio Brevetti, via Piave 18, I-21041 Albizzate (VA) (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BOHUS, Peter [HU/HU]; Mikszáth Kálmán Utca 3, H-8000 Székesfehérvár (HU). DI MODUGNO, Rocco [IT/IT]; Via San Damiano, 36, I-20034 Giussano (MB) (IT). PAGANINI, Gianfranco [IT/IT]; Via Magellano, n. 1, I-20020 Magnago (MI) (IT). PICCO, Cristina [IT/IT]; Piazza Borromeo, 39, I-20020 Nosate (MI) (IT). LI BASSI, Giuseppe [IT/IT]; Via Stretti, 4, I-21026 Gavirate (VA) (IT).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: AQUEOUS HERBICIDE CONCENTRATE

(57) Abstract: Stable aqueous herbicide concentrate composition containing potassium, ammonium or isopropylamine salts of glyphosate and anionic esters of alkyl polyglycosides containing a sulfated sulfonic acid group.



WO 2011/000880 A2

AQUEOUS HERBICIDE CONCENTRATE

FIELD OF THE INVENTION

The present invention relates to stable aqueous herbicide concentrate compositions containing potassium, ammonium or
5 isopropylamine salts of glyphosate and anionic esters of alkyl polyglycosides containing a salified sulfonic acid group.

BACKGROUND OF THE ART

Agrochemical active ingredients - according to the characteristics of the actives and of their intended applications - can be
10 formulated as dusts, wettable powders, dispersible granules, suspension concentrates, emulsions and concentrated solutions, and their application as formulated products is generally carried out with aqueous spray in the form of solution, suspension or emulsion.

15 Surfactants are commonly used in order to disperse and suspend the solid substances, or to emulsify the oily liquids in water, forming stable suspensions or emulsions. The surfactants help the formation of aqueous dispersions of compounds insoluble in water. Moreover the surfactants reduce the interface tension between aqueous
20 spray and the material (soil, seeds, foliage) to be treated, thus favoring the spreading of droplets on the treated surface and the penetration of the active ingredient into the materials.

Among surfactants, which can be used for the afore mentioned purposes, aliphatic nonionic alkylpolyglycosides have been known for a long time. These materials offer several advantages due to their low toxicity and good biodegradability, especially if

5 compared with the ethoxylated fatty amines, which are widely used as adjuvant for glyphosate but create concern for their aquatic toxicity. Due to these features, the organic polyglycosides provide, in agrochemical formulations and applications, a wider spectrum of functions, since other equivalent traditional adjuvants

10 are normally used only as wetting agents and/or emulsifiers. For instance, US 4,888,325 describes pesticide compositions that contain alkylglycosides, alone or in combination with other surfactants.

However, such compositions show weak wetting performance

15 and cannot sufficiently reduce the interfacial tension between the aqueous spray and the material on which said spray are applied. US 5,385,750 describes the use of aliphatic alkylpolyglycosides as co-adjuvant in pesticide formulations in combination with a fatty alcohol.

20 According to US 5,385,750 the addition of a fatty alcohol to the alkylpolyglycosides increases its wetting performance, favoring the penetration of the pesticide active ingredient into biological

materials, even when the treated surface layers are waxy or oily as in the case of foliage.

On the other hand, the presence of a fatty alcohol creates considerable drawbacks: it gives bad odors and causes a
5 noticeable lowering of the emulsifying ability of the alkylpolyglycosides.

It is known from EP 1 179 979 how to obtain agrochemical compositions based on anionic alkylpolyglycosides that have better wetting properties and maintain suitable emulsifying
10 characteristic, without the above described disadvantages of the nonionic alkylpolyglycosides.

US 7,316,990 (corresponding to US 2005/032649) describes herbicidal formulations containing high concentrations of glyphosate monomethylamine or dimethylamine salt and one or
15 more surfactants selected from a long list of nonionic, ionic and cationic surfactants. Both nonionic alkylpolyglycosides and anionic ester derivatives of alkylpolyglycosides, in particular the citrate and tartrate esters, are used in the examples for the preparation of concentrated formulations of these specific glyphosate salts,
20 which exhibit high stability and significantly lower viscosity at high concentrations.

Anionic esters of alkylpolyglucosides bearing a (not better detailed) residue from sulfosuccinic acid are also reported among

the utilizable surfactants, but they are not exemplified nor preferred.

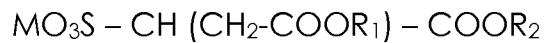
We have now discovered that concentrated aqueous formulations of potassium, ammonium and isopropylamine salts of N-(phosphonomethyl) glycine (glyphosate) comprising specific non-polyalkoxylated anionic esters of alkyl polyglycosides containing a sulfonated sulfonic acid group are stable and can incorporate a higher amount of the anionic ester of alkylpolyglycosides; moreover they can be used to prepare in locus diluted sprayable formulations, without showing the crystallization problems that rise with other surfactants.

This is especially surprising in view of the fact that concentrated formulations containing the potassium, ammonium and isopropylamine salts of N-(phosphonomethyl) glycine (glyphosate) and an anionic ester of alkylpolyglycosides derived from citric and tartaric acid show poor stability.

SUMMARY OF THE INVENTION

It is therefore an object of the present invention an aqueous herbicide composition containing from 100 to 750 g/l (as acid equivalent) of potassium, ammonium or isopropylamine salts of glyphosate and from 1 to 50%, preferably from 2 to 20%, by weight of anionic esters of linear or branched C₆-C₂₀ alkylpolyglycosides having the formula (I):

5



(I)

wherein:

M is an organic or inorganic cation such as Na, K, NH₄ or mono-,
 5 di-, tri-alkanolammonium or mixture thereof;

R₁ is the group:



which is connected to the acyl group through the residue Z, and

wherein

10 Z represents the residue of a hexose, pentose or sorbitol,

R is an alkyl containing from 6 to 20 carbon atoms,

m is 0 or 1,

p is a number from 1 to 10;

R₂ is M or R₁.

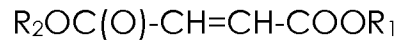
15 DETAILED DESCRIPTION OF THE INVENTION

The aqueous herbicide concentrate of the present invention comprises at least 10% by weight, preferably from 20 to 60% by weight, of water.

Preferably, in formula (I) M is Na or K, R is a linear or branched alkyl
 20 group containing from 8 to 14 carbon atoms, Z is the residue of glucose, m is 0 and p is between 1 and 5.

The anionic esters of linear or branched C₆-C₂₀ alkylpolyglycosides having the formula (I) are known from EP 510565; they may be

prepared by a process that comprises the sulfonation of the correspondent maleic diesters or monoesters of the formula:



as described in more detail in the same patent.

- 5 In the most preferred embodiment, the anionic esters of alkylpolyglycosides are synthesized from alkylpolyglucosides having an average degree of polymerization between 1.0 and 2.5, i.e., preferably, in formula (I) p is between 1.0 and 2.5. This anionic esters are environmentally friendly and derived from
10 renewable resources.

In the preferred embodiments the aqueous herbicide concentrate is a homogeneous solution and comprises from 300 to 700 g/l, more preferably from 400 to 655 g/l (as acid equivalent), of potassium, ammonium or isopropylamine salts of glyphosate.

- 15 The aqueous herbicide composition of the invention may further contain:

- other surfactants, such as nonionic alkylpolyglycosides, ethoxylated fatty alcohols, anionic esters of fatty alcohols, C₆-C₁₈ alkyldimethyl betaine.
- 20 • other herbicides, such as salts of glufosinate, bentazon, 2,4-D, dicamba, MCPA, MCPP, MCPB, amitrol, metconazol, clopyralid, dichlorprop, imazalil, picloram, and mixtures thereof;

- water soluble organic solvents, such as glycerol, ethylene glycol, propylenglycole, dipropylene glycol methyl ether (Dowanol DPM), dipropylene glycol, butyldiglycol, dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone, 5 dibutoxymethane (butylal), methanol, ethanol, isopropanol, ethyl lactate (purasolv), propylene carbonate and mixture thereof;
- other usual additives of agrochemical compositions, such as antifoam agents, antifreeze agents, dyes, stabilizers, buffers, 10 thickeners, flow enhancers, wetting agents, lubricants, fillers, drift control agents, deposition enhancers, evaporation retardants and the like.

The aqueous herbicide compositions according to the invention are useful for the treatment of plants and of any other biologic 15 material which requires the application of herbicides.

Preferably, said concentrated herbicide composition is used in diluted form, as aqueous spray formulations which include from 0.001% to 3% of active ingredient and, optionally, other concentrated preparations of active ingredients, micronutrients, 20 other surfactants and/or other additives commonly used in the agrochemical compositions.

The Applicant has found that, in aqueous spray herbicide formulations, the use of anionic esters of alkylpolyglycoside

containing a salified sulfonic acid group according to formula (I) can help the formation of a homogeneous dispersion of the herbicide in water, thus accelerating the penetration of active ingredient in the treated biological materials .

- 5 Optionally, the aqueous spray formulations can also include drift control agents, humectants, corrosion inhibitors, microbial inhibitors, pH adjusters, anti-foam agents or mixture thereof.

The following Examples serve to illustrate the stability of concentrated aqueous herbicide compositions according to the
10 invention. A comparison is made with analogous compositions prepared from known anionic alkylpolyglycosides and from other surfactants that are known to efficiently perform as stabilizer of concentrated glyphosate compositions.

EXAMPLES.

- 15 – Preparation of concentrated aqueous herbicide compositions of glyphosate isopropylamine salt (glyphosate IPA) with different surfactants.

The compositions of Example 1- 12 were prepared by blending at room temperature an aqueous concentrate of glyphosate IPA 62%
20 wt with the appropriate amount of surfactant and water as reported in Table 1 and 2.

Eucarol AGE/EC is a coco alkylpolyglucoside citric ester (Lamberti),
30% in water

Eucarol AGE/SS is a coco alkylpolyglucoside sulfosuccinic ester
(Lamberti), 45 % in water

5 PIC 255 is a isodecyl alkylpolyglucoside sulfosuccinic ester, 50% in
water

PIC 244 is a linear C8 - C10 alkylpolyglucoside sulfosuccinic ester,
50% in water

PIC 265 is a linear C10 and 2-ethylhexyl alkylpolyglucoside citric
10 ester, 40% in water

PIC 263 is a linear C10 and 2-ethylhexyl alkylpolyglucoside ,
sulfosuccinic ester, 50% in water

PIC 245 is a linear C8 - C10 alkylpolyglucoside citric ester, 40% in
water

15 Emulson CB 30 is an alkyl dimethyl betaine, 30% in water (Lamberti)

Emulson AG/GPE3/CA is a ethoxylated tallow amine (15 moles)
80% in isobutyl alcohol (Lamberti)

Emulson AG/GPE3/SSM is a ethoxylated tallow amine (15 moles)
70% in ethylene glycol and polyethylene glycol 200 (Lamberti)

Table 1

Component %	Ex. 1*	Ex.2	Ex.3	Ex.4	Ex.5*	Ex.6
Water	22,20	22,20	22,20	22,20	22,20	22,20
Eucarol AGE/EC	10,30					
Eucarol AGE/SS		10,30				
PIC 255			10,30			
PIC 244				10,30		
PIC 265					10,30	
PIC 263						10,30
Glyphosate IPA 62%	67,50	67,50	67,50	67,50	67,50	67,50

* Comparative

Table 2

Component %	Ex. 7*	Ex. 8*	Ex. 9*	Ex. 10*	Ex.11	Ex.12*
Water	22,20	22,20	22,20	22,20	22,20	22,20
Eucarol AGE/SS					2,60	
PIC 245	10,30					
Emulson CB 30		10,30			7,70	5,15
Emulson AG/GPE3/CA			10,30			5,15
Emulson AG/GPE3/SSM				10,30		
Glyphosate IPA 62%	67,50	67,50	67,50	67,50	67,50	67,50

* Comparative

Tables 3 and 4 report the characteristics of the concentrated herbicide compositions of Examples 1-12 and the aqueous spray formulations prepared thereof by dilution with water.

- 5 All the concentrated aqueous herbicide compositions of the invention are clear and homogeneous liquids. These compositions are stable for at least one week at 0 °C and at least 2 weeks at 54 °C with no phase separation or crystallization. Also the aqueous spray formulations prepared from the compositions of the
- 10 invention are stable and can be stored for at least one day without any problem.

Table 3

Characteristic	Example 1*	Example 2	Example 3	Example 4	Example 5*	Example 6
A.I. content (acid equivalent)	360 g/l	360 g/l	360 g/l	360 g/l	360 g/l	360 g/l
Density	1,17 g/ml	1,17 g/ml	1,17 g/ml	1,17 g/ml	1,17 g/ml	1,17 g/ml
Appearance	Crystals	Clear liquid	Clear liquid	Clear liquid	Clear liquid	Clear liquid
Stability (7 days at 0°C)		No crystals	No crystals	No crystals	No crystals	No crystals
Stability (15 days at 54°C)		No crystals	No crystals	No crystals	No crystals	No crystals
Appearance (sol. 5% t = 5h)		Clear liquid	Clear liquid	Clear liquid	Cloudy liquid	Clear liquid
Appearance (sol. 5% t = 24h)		Clear liquid	Clear liquid	Clear liquid	Crystals	Clear liquid

* Comparative

Table 4

Characteristic	Example 7*	Example 8*	Example 9*	Example 10*	Example 11	Example 12*
A.I. content (acid equivalent)	360 g/l	360 g/l	360 g/l	360 g/l	360 g/l	360 g/l
Density	1,17 g/ml	1,17 g/ml	1,17 g/ml	1,17 g/ml	1,17 g/ml	1,17 g/ml
Appearance	Clear liquid	Clear liquid	Clear liquid	Clear liquid	Clear liquid	Clear liquid
Stability (7 days at 0°C)	No crystals	No crystals	No crystals	No crystals	No crystals	No crystals
Stability (15 days at 54°C)	No crystals	No crystals	No crystals	No crystals	No crystals	No crystals
Appearance (sol. 5%, t = 5h)	Cloudy liquid	Clear liquid	Clear liquid	Clear liquid	Clear liquid	Clear liquid
Appearance (sol. 5% t = 24h)	Crystals	Clear liquid	Clear liquid	Clear liquid	Clear liquid	Clear liquid

* Comparative

5 Examples 13-19

Compositions of Example 13-19 were prepared by blending at room temperature a concentrate solution of glyphosate IPA 62% or a concentrate solution of glyphosate potassium salt 69% or 61% (glyphosate K) with the appropriate amount of surfactant and

10 water as reported in Tables 5 and 6.

Table 5

Component %	Ex. 2	Ex.13	Ex. 14	Ex. 15	Ex. 16
Water	22.2	13.5	18.0	3,6	32
Glyphosate-IPA 62%	67.5	66.4		86,4	24
Glyphosate K61%			71.1		
2,4-D DMA (49%)					27
Eucarol AGE SS	10.3	20.1	10.9	10,0	17

Table 6

Component %	Ex. 17	Ex.18	Ex. 19
Water		18.4	10.3
Glyphosate-IPA 62%		66.4	
Glyphosate K 61%	90		78.8
PIC 244	10		10.9
Eucarol AGE SS		15.2	

5

Table 7 and 8 report the characteristics of the concentrate herbicide compositions of Examples 2, 13-19. The viscosity of the compositions was measured with a Brookfield™ LVT viscometer.

Table 7

Characteristic	Example 2	Example 13	Example 14	Example 15	Example 16
A.I. content (glyphosate acid equivalent)	360 g/l	360 g/l	480 g/l	480 g/l	130 g/l
Density	1,17 g/ml	1,19 g/ml	1,35 g/ml	1,20 g/ml	1,18 g/ml
Appearance	Clear liquid	Clear liquid	Clear liquid	Clear liquid	Clear liquid
Stability (25 °C; 720 days)	No crystals	No crystals	No crystals	No crystals	No crystals
Stability (0 °C; 7 days)	No crystals	No crystals	No crystals	No crystals	No crystals
Viscosity (spindle N° 1, 5 rpm, 25°C)	37,7 mPa*s	39,2 mPa*s	35,0 mPa*s	48,0 mPa*s	30,5 mPa*s

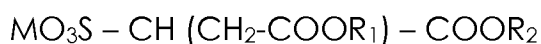
All the concentrate aqueous herbicide compositions of Examples
5 13-19, according to the invention, are clear and homogeneous
liquids. These compositions are stable for at least 720 days at 25 °C
with no phase separation or crystallization. Moreover the viscosity
of the compositions are very low so they can be poured and
mixed with other substances or solvents quite easily.

Table 8

Characteristic	Example 17	Example 18	Example 19
A.I. content (glyphosate acid equivalent)	655 g/l	360 g/l	540 g/l
Density	1.47 g/ml	1,18 g/ml	1,37 g/ml
Appearance	Clear liquid	Clear liquid	Clear liquid
Stability (25 °C; 720 days)	No crystals	No crystals	No crystals
Stability (0 °C; 7 days)	No crystals	No crystals	No crystals
Viscosity (spindle N° 1, 5 rpm, 25°C)	95,0 mPa*s	39,2 mPa*s	35,0 mPa*s

CLAIMS

1. Aqueous herbicide composition containing from 100 to 750 g/l (as acid equivalent) of potassium, ammonium or isopropylamine salts of glyphosate and from 1 to 50%, preferably from 2 to 20%, by weight of anionic esters of linear or branched C₆-C₂₀ alkylpolyglycosides having formula (I):



(I)

wherein:

M is an organic or inorganic cation such as Na, K, NH₄ or mono-, di-, tri-alkanolammonium or mixture thereof;

R₁ is the group:



which is connected to the acyl group through the residue Z,

and wherein

Z represents the residue of a hexose, pentose or sorbitol,

R is an alkyl containing from 6 to 20 carbon atoms,

m is 0 or 1,

p is a number from 1 to 10;

R₂ is M or R₁.

2. The aqueous herbicide composition according to claim 1, comprising at least 10% by weight of water.

3. The aqueous herbicide composition according to claim 2. comprising from 20 to 60% by weight of water.
4. The aqueous herbicide composition according to claim 1. or 2. or 3. comprising from 2 to 20% by weight of the anionic esters of linear or branched C₆-C₂₀ alkylpolyglycosides and from 400 to 655 g/l (as acid equivalent) of the glyphosate salts.
5. The aqueous herbicide composition according to claim 4. wherein in formula (I) M is Na or NH₄, R is a linear or branched alkyl group containing from 8 to 14 carbon atoms, Z is the residue of glucose, m is 0 and p is between 1 and 5.
6. The aqueous herbicide composition according to claim 5. wherein in formula (I) p is between 1 and 2.5.
7. The aqueous herbicide composition according to claim 6. further containing one or more surfactants selected among nonionic alkylpolyglycosides, ethoxylated fatty alcohols, anionic esters of fatty alcohols, C₆-C₁₈ alkyldimethyl betaine.
8. The aqueous herbicide composition according to claim 6. further containing a water soluble organic solvent.
9. The aqueous herbicide composition according to claim 6. further containing one or more other herbicides different from the glyphosate salts.

10. The aqueous herbicide composition according to claim 6.
further containing one or more additives selected among
antifoam agents, antifreeze agents, dyes, stabilizers, buffers,
thickeners, flow enhancers, wetting agents, lubricants, fillers,
drift control agents, deposition enhancers, evaporation
retardants.