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High-strength, low viscosity herbicidal concentrate of clopyralid dimethylamin

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ABSTRACT:

This invention relates to a high-strength, aqueous herbicidal concentrate containing the clopyralid dimethylamine salt. The formulation is stable to storage and exhibits lower viscosity than other clopyralid amine salt formulations.

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COMPLETE SPECIFICATION STANDARD PATENT

Invention Title: **High-strength, low viscosity herbicidal concentrate of clopyralid dimethylamin**

The following statement is a full description of this invention, including the best method of performing it known to us:

**HIGH-STRENGTH, LOW VISCOSITY HERBICIDAL
CONCENTRATE OF CLOPYRALID DIMETHYLAMINE**

This invention concerns a high-strength, low viscosity aqueous concentrate of the herbicide clopyralid dimethylamine.

5 Clopyralid, 3,6-dichloropicolinic acid, is an herbicide used to control broadleaf weeds in cereal crops, pasture, fallow, forest and industrial situations. Various formulations are currently marketed, many of which are aqueous solutions that are normally diluted prior to use. Typically the clopyralid is provided as an amine salt, which exhibits sufficiently high solubility in water to provide an aqueous concentrate herbicidal formulation (SL). Typical
10 commercial formulations of clopyralid have an active loading of from 300 grams acid equivalent per liter (gae/l) to 450 gae/L of the monoethanolamine (MEA) or triisopropanolamine (TIPA) salts. Lontrel[®] herbicide (registered trademark of Dow AgroSciences LLC) is sold as a 360 gae/L SL formulation of the monoethanolamine salt of clopyralid in water and is used for the control of broadleaf weeds in turf and ornamentals.

15 High-strength formulations are desirable for a variety of economic and environmental reasons. For example, it is desirable to provide a high-strength concentrate in order to reduce shipping and handling costs and to reduce the amount of packaging material that must be disposed after use of the product. The high-strength concentrates should be stable and retain potency during storage and shipping. Furthermore, the high-strength concentrate should be a
20 clear, homogeneous liquid that is stable at temperatures at least as high as 54 °C and should not exhibit any precipitation of solids at temperatures as low as -10 °C.

There is a continuing need for new, high-strength SL herbicidal formulations that exhibit low viscosity and stability at low temperatures.

25 It has now been found that use of the dimethylamine (DMA) salt of clopyralid allows the preparation of a high-strength, aqueous concentrate of surprisingly low viscosity. More particularly, the present invention provides a high-strength herbicidal aqueous concentrate comprising: (a) water and (b) clopyralid, in the form of the DMA salt, in solution in the water in an amount of from 450 grams of acid equivalent per liter (gae/l) to 850 gae/L of the total composition.

In an effort to increase the active ingredient loading of an SL clopyralid formulation, it has been discovered that the DMA salt of clopyralid can create a physically stable concentrate containing greater than 600 gae/L, preferably greater than 750 gae/L, at -10 °C. Furthermore, the concentrates produced from the clopyralid DMA salt have a much lower viscosity than other clopyralid amine salt SL formulations of lower concentration.

Aqueous concentrates of the commonly used amine salts of clopyralid can become increasingly viscous, particularly at lower temperatures, at concentrations of greater than 400 gae/l, particularly at concentrations of greater than 450 gae/l. The high viscosity makes the aqueous concentrates difficult to measure and pump, especially at lower temperatures that may be encountered at the beginning of the growing season.

In another embodiment, the present invention provides a method of treating plants with the herbicidal concentrate. The concentrate is typically applied to the plants post-emergently either as a concentrated solution or, preferably, as a more diluted solution with water.

In general the present invention is directed to a high-strength aqueous herbicidal concentrate composition containing the DMA salt of clopyralid. More specifically, the present invention provides a high-strength herbicidal concentrate composition comprising: (a) water, and (b) clopyralid, in the form of the DMA salt, in solution in the water in an amount of from 450 gae/l to 850 gae/L of the total composition. In preferred embodiments, the high-strength herbicidal formulation includes greater than 600 gae/l based upon the clopyralid acid equivalent of the clopyralid salt; more preferably, the high-strength herbicidal formulation includes greater than 750 gae/l based upon the clopyralid acid equivalent of the clopyralid salt.

The present invention provides a high-strength herbicidal concentrate that is storage stable at high temperatures. That is, the concentrate forms a clear, homogeneous, stable solution that does not exhibit cloudiness under the storage conditions. More preferably, the concentrates of the present invention are stable at temperatures of greater than or equal to 40 °C, more preferably, at temperature equal to or greater than 55 °C.

Furthermore, the herbicidal concentrate also does not exhibit separation or precipitation (or crystallization) of any of the components at low temperatures. For example,

the high-strength concentrate remains a clear solution at temperatures below 0 °C, more preferably at temperatures below -5 °C and most preferably at a temperature equal to or less than -10 °C.

The high-strength herbicidal concentrates of the DMA salt of clopyralid are surprisingly less viscous than even less concentrated compositions of other salts of clopyralid. In preferred embodiments, the herbicidal concentrates of the present invention exhibit a viscosity of less than 50 centipoise (50 mPa-s), even at temperatures as low as 5 °C.

The concentrate described herein can be applied to plants in an amount sufficient to induce an herbicidal effect. For example, a concentrate prepared according to the present invention can be applied as a diluted aqueous solution to plants including the plants' leaves, stems, branches, flowers and/or fruit. The herbicidal formulation can be applied in an herbicidally effective amount sufficient to inhibit plant growth or kill individual plants.

The concentrate of the present invention may also be mixed with or applied with other herbicides. Suitable herbicides which may be mixed with or applied with the composition of the present invention to control plant growth include, but are not limited to, 2,4-D esters and amines, acetochlor, aclonifen, amidosulfuron, aminocyclopyrachlor, aminopyralid, aminotriazole, ammonium thiocyanate, asulam, atrazine, beflubutamid, benazolin, bentazone, bifenox, bromacil, bromoxynil, butachlor, butafenacil, butralin, butroxydim, carbetamide, carfentrazone, carfentrazone-ethyl, chlormequat, chlorsulfuron, chlortoluron, cinidon-ethyl, clethodim, clodinafop-propargyl, clomazone, clopyralid, cyanazine, cyclosulfamuron, cycloxydim, dicamba, dichlobenil, dichlorprop-P, diclofop-methyl, diflufenican, diflufenzopyr, dimefuron, dimethachlor, diquat, diuron, EPTC, ET-751, ethoxysulfuron, fenoxaprop, fenoxaprop-ethyl, fenoxaprop-ethyl + isoxidifen-ethyl, fenoxaprop-p-ethyl, flazasulfuron, florasulam, fluazifop, fluazifop-P-butyl, flucarbazone, flucetosulfuron (LGC-42153), flufenacet, flumetsulam, flumioxacin, flupyrsulfuron, fluroxypyr, fluroxypyr meptyl, flurtamone, glufosinate, glufosinate-ammonium, glyphosate, haloxyfop-methyl, haloxyfop-R, hexazinone, imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, indanofan, iodosulfuron, iodosulfuron-ethyl-sodium, ioxynil, isoproturon, isoxaben, isoxaflutole, KIH-845, lactofen, linuron, MCPA, mecoprop-P, mesosulfuron, mesosulfuron-ethyl sodium, metazochlor, metosulam, metribuzin, metsulfuron, metsulfuron-methyl, MSMA, napropamide, norfurazon, orthosulfamuron, oryzalin, oxadiargyl, oxadiazon,

oxyfluorfen, paraquat, pendimethalin, penoxsulam, picloram, picolinafen, pinoxaden, primisulfuron, profluzol, propaquizafop, propoxycarbazone, propyzamide, prosulfocarb, prosulfuron, pyraflufen ethyl, pyrasulfotole, pyribenzoxim (LGC-40863), pyroxsulam, quinmerac, quizalofop-ethyl-D, quizalofop-P-ethyl, quizalofop-p-tefuryl, sethoxydim, simazine, sulfentrazone, sulfosate, sulfosulfuron, tebuthiuron, tepraloxidim, terbacil, terbutryn, thiazopyr, thifensulfuron, thifensulfuron-methyl, topramezone, tralkoxydim, triasulfuron, tribenuron, tribenuron-methyl, triclopyr and trifluralin.

The herbicidal compositions prepared according to the present invention are highly effective against a variety of weeds. The concentrate of the present invention can be used as is or combined with other components including other agriculturally acceptable adjuvants commonly used in formulated agricultural products, such as antifoam agents, compatibilizing agents, sequestering agents, neutralizing agents and buffers, corrosion inhibitors, dyes, odorants, penetration aids, wetting agents, spreading agents, dispersing agents, thickening agents, freeze point depressants, antimicrobial agents, crop oil, safeners and the like. The concentrated agricultural formulations are typically diluted in water and then applied by conventional means well known to those skilled in the art.

As used herein, except where the context requires otherwise the term 'comprise' and variations of the term, such as 'comprising', 'comprises' and 'comprised', are not intended to exclude other additives, components, integers or steps.

Example 1: Preparation of a High-Strength Clopyralid DMA Salt Formulation

A high-strength clopyralid DMA salt concentrate was prepared by reacting a mixture of clopyralid acid technical and water with just enough aqueous dimethylamine solution to neutralize the clopyralid. Following addition of the blue dye Hexaran Brilliant Blue Supra and dilution with water, a 600 gae/L formulation of the clopyralid DMA salt was obtained. The example described in Table 1 demonstrates the invention.

Table 1. Clopyralid DMA 600 gae/L Formulation

Component	Role	AI	AI (wt%)	AE
clopyralid	active ingredient	600 g/L	49.18% w/w	600 g/L
Hexaran Brilliant Blue Supra	color dye	0.25 g/L	0.02% w/w	
dimethylamine	neutralizer	140.94 g/L	11.55% w/w	
water	solvent	478.81 g/L	39.25% w/w	

Example 2: Viscosity of High-Strength Clopyralid DMA Salt Formulation

The viscosity of sample formulations was measured with a TA Instruments AR 2000 rheometer. Table 2 lists the viscosity measured for the concentrate described in Example 1 and compares it to a commercial clopyralid TIPA 300 gae/L formulation (Dow AgroSciences Australia Ltd.) over a temperature range of 5 to 25 °C. The viscosity of the high-strength clopyralid DMA salt concentrate was significantly lower than the clopyralid TIPA commercial concentrate, particularly at the lower temperatures.

Table 2. Comparison of the Viscosities of Clopyralid DMA 600 gae/L and Clopyralid TIPA 300 gae/L Concentrates at 5 to 25 °C

Temperature °C	Viscosity (mPa.s)	
	clopyralid DMA (600 gae/L)	clopyralid TIPA (300 gae/L)
5	33	50
10	29	37
15	22	28
20	18	21
25	15	17

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Example 3: Stability of High-Strength Clopyralid DMA Salt Concentrates to Low Temperature

Several crystallization studies have been conducted on the high-strength clopyralid DMA concentrates using several sources of active ingredient. Three batches of clopyralid technical from two sources were converted into high-strength clopyralid DMA sample concentrates and these were seeded with active ingredient crystals and stored for 6 days at -10 °C. All samples remained physically stable (no crystallization) and were clear, homogeneous liquids. The concentrations of these samples ranged from 783 gae/L to 850 gae/L of clopyralid DMA.

10 Example 4: Herbicidal Efficacy of High-Strength Clopyralid DMA Salt Concentrate

The high-strength clopyralid DMA salt concentrate was evaluated for efficacy against capeweed (AROCA) in field trials. Table 3 shows the biological efficacy of the 630 gae/l clopyralid DMA salt concentrate compared to a commercial concentrate of Lontrel® Herbicide containing clopyralid TIPA salt at a concentration of 300 gae/L. Across all application rates the high-strength clopyralid DMA salt concentrate showed nearly equivalent performance to the commercial clopyralid TIPA salt formulation.

Table 3. Comparison of High-Strength Clopyralid DMA (630 gae/L) and Lontrel® Herbicide (clopyralid TIPA 300 gae/L) at Equivalent Rates for Control of Capeweed (AROCA)

Treatment	Formulation Concentration (gae/L)	Application Rate (gae/ha)	% Control of Capeweed*
clopyralid DMA	630	22	67
clopyralid TIPA	300	22	63
clopyralid DMA	630	43	87
clopyralid TIPA	300	45	84
clopyralid DMA	630	86	94
clopyralid TIPA	300	90	91
clopyralid DMA	630	180	99
clopyralid TIPA	300	180	98

20 * average of six trials

AROCA

Arctotheca calendula

capeweed

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What is claimed is:

5 1. Use of a high-strength herbicidal aqueous concentrate comprising: (a) water and (b) clopyralid, in the form of the dimethylamine (DMA) salt, in solution in the water in an amount of from 450 grams of acid equivalent per liter (gae/L) to 850 gae/L of the total composition, for formulating a herbicidal composition for controlling undesirable vegetation.

2. The use of Claim 1 wherein said high-strength herbicidal aqueous concentrate contains greater than 600 gae/L of the clopyralid DMA salt.

3. The use of Claim 1 or Claim 2 wherein said high-strength herbicidal aqueous concentrate has a viscosity less than 50 centipoise at low temperature.

0 4. A method of controlling undesirable vegetation which comprises applying to the vegetation a diluted aqueous solution of a herbicidal composition comprising:

(a) water;

(b) clopyralid;

(c) DMA

15 wherein said DMA and clopyralid are dissolved in the water of the herbicidal composition; and

wherein said clopyralid is provided in the herbicidal composition in an amount from 450 to 850 gae/L of the total composition.

5. The method of Claim 4 wherein said clopyralid is provided in the herbicidal composition in an amount of greater than 600 gae/L of the total composition.

20 6. The method of Claim 4 wherein said clopyralid is provided in the herbicidal composition in an amount of greater than 750 gae/L of the total composition.

7. The method of Claim 4 wherein said clopyralid is provided in the herbicidal composition in an amount of 600 gae/L of the total composition.

25 8. The method of Claim 4 wherein said clopyralid is provided in the herbicidal composition in an amount of from 783 to 850 gae/L of the total composition.

9. The method of Claim 4 wherein said clopyralid is provided in the herbicidal composition in an amount of 630 gae/L of the total composition.
10. A method of controlling undesirable vegetation which comprises applying to the vegetation a diluted aqueous solution of a high-strength herbicidal aqueous concentrate comprising: (a) water and (b) clopyralid, in the form of the dimethylamine (DMA) salt dissolved in the water of the concentrate in an amount of 630 gae/L, wherein the clopyralid in the diluted aqueous solution is applied at an application rate of from 22 grams acid equivalent per hectare (gae/ha) to 180 gae/ha.
11. The method of Claim 10, wherein the clopyralid is applied at an application rate of 22 gae/ha.
12. The method of Claim 10, wherein the clopyralid is applied at an application rate of 43 gae/ha.
13. The method of Claim 10, wherein the clopyralid is applied at an application rate of 86 gae/ha.
14. The method of Claim 10, wherein the clopyralid is applied at an application rate of 180 gae/ha.
15. The method of any one of Claims 1 to 14 wherein the undesirable vegetation is capeweed.
16. The use of Claim 1, substantially as herein described.
17. The method of Claim 10, substantially as herein described.