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**Abstract**

A contradeglutitious solid herbicidal composition comprising a 1,1'-dimethyl-4,4'-dipyridylum salt and a thickening agent. This composition is difficult to swallow in its original form or even when diluted in a glass of water. The composition does not impair the inherent herbicidal effects and applicability of paraquat.
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DESCRIPTION

TITLE OF THE INVENTION

CONTRADEGLUTITIOUS SOLID HERBICIDAL COMPOSITION

BACKGROUND OF THE INVENTION

The present invention relates to a contradeglutitious solid herbicidal composition (i.e., a herbicidal composition not easy to swallow). More specifically, it relates to a contradeglutitious solid herbicidal composition containing, as a herbicidal agent, a 1,1'-dimethyl-4,4'-dipyridylum salt (i.e., so-called "paraquat"), which is not easily swallowed even if such a paraquat solution is accidentally or intentionally drunk.

The importance of herbicides or pesticides in modern agriculture is widely recognized and many herbicides or pesticides are in practical use. Herbicides or pesticides practically used must be registered, after being subjected to a severe examination including the toxicity and safety thereof based on the laws and regulations concerned. Accordingly, as long as herbicides or pesticides are properly used according to instructions for use, they will not harm the human body in any way. However, the present status is such that toxic or poisonous accidents caused by a portion of herbicides or pesticides still occur in spite of the fact that the proper handling of herbicides or pesticides and the preventing of injury thereby to the human body has been taught and the dangers of improper usage have been widely announced for a long time. In particular, a herbicide, paraquat, is widely used because of the strong herbicidal effect and easy applicability thereof, and quite a large number of toxic or poisonous accidents have been caused by the accidental or intentional drinking of paraquat despite clear indications of its toxicity. This is because paraquat has very strong acute toxicity and is commercially available in the form
of an aqueous solution having a relatively high concentration.

Paraquat is generally marketed as an about 20% to 30% aqueous solution. When used, the raw paraquat solution is diluted 300 to 1500 times with water and the resultant diluted paraquat solution is generally sprayed as a weed-killer in an amount of 100 to 150 liters per 10 are (i.e., 100 m²). The oral acute toxicity of paraquat is an LD₅₀ of 166 to 217 mg/kg (rat) and it is reported in "Kyukyu Igaku" 4(4), p 399 (1980) that the lethal dose of paraquat for humans is approximately 15 ml of the 20% aqueous solution. On the other hand, it is reported in "Gekkan Yakuji" 25(8), p 147 (1983) that an average amount drunk in one mouthful by an adult human is generally approximately 40 ml. This means that, if a commercially available paraquat solution is accidentally or intentionally drunk, a mouthful of the paraquat solution is sufficient to be lethal to a human.

Various attempts have been made to prevent accidental toxic or poisonous injury caused by paraquat. For example, odorants or colorants are mixed into the paraquat solutions to prevent accidental drinking by giving it an unpleasant odor or color. However, this is not effective for infants or against intentional drinking. Furthermore, the inclusion of nauseants in the paraquat solutions has been proposed, to rapidly remove the mistakenly drunk paraquat from the stomach and other digestive system prior to the absorbance of paraquat into the body therethrough. However, it is extremely unfortunate that, at present, once paraquat is swallowed, a reliable and effective curing or treatment method is not available, although this depends upon the amount swallowed, even if the paraquat is vomited at an early stage.

Consequently, although various attempts have been made to solve the above-mentioned problems, an appropriate and effective means has not, as yet, been
found. In order to prevent toxic or poisonous accidents caused by the oral intake of paraquat, it is thought that the concentration of commercially available paraquat should be decreased so that a lethal amount is not reached unless a relatively large amount of a paraquat solution is drunk. However, this causes disadvantages in the transportation and storage of paraquat solutions and also impairs the inherent easy handling characteristics of paraquat. On the other hand, it is considered that, when paraquat is marketed in the form of a solid instead of an aqueous solution, the paraquat becomes difficult to drink, toxic or poisonous injuries caused by the accidental intake of paraquat can be prevented, and, furthermore, the transportation and storage thereof are convenient. However, since paraquat is completely soluble in water, an aqueous solution containing a lethal amount of paraquat is easily prepared from such solid paraquat with a mouthful of water, it would be difficult to prevent to take the poison with suicidal intent.

SUMMARY OF THE INVENTION

Accordingly, the objects of the present invention are to eliminate the above-mentioned disadvantages of paraquat and to provide a contradeglutitious solid herbicidal composition capable of effectively preventing the occurrence of accidents or injuries from acute poisoning caused by an accidental or intentional intake of paraquat, without impairing the essential characteristics, e.g., strong herbicidal effects and easy applicability, of paraquat.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided a contradeglutitious solid herbicidal composition comprising a 1,1'-dimethyl-4,4'-dipyridylum salt and a thickening agent.

DESCRIPTION OF THE PREFERRED EMBODIMENTS
According to the present invention, since the herbicidal composition is in a solid form and contains a thickening agent, it is difficult to swallow in the solid form itself and, if an amount of the composition corresponding to a lethal does to human beings is dissolved in a glass of water, only a non-fluidizable mixture, which is difficult to swallow, is obtained. Of course, the present solid herbicidal composition can be changed to an aqueous solution by diluting the composition with a large amount of water. However, since the paraquat concentration of this diluted solution is very low, a lethal amount cannot be ingested unless a remarkably large amount of the diluted solution is drunk. This is practically difficult and the effects of nauseants can be utilized to decrease the likelihood of death from such ingestion. Furthermore, since the present solid herbicidal composition can be stored and transported in glass and plastic vessels, and since the present solid herbicidal composition can be used on-site by diluting with water, there is no substantial difference between the present solid herbicidal composition and conventional commercially available paraquat solutions in the transportation, handling, and applicability thereof. When diluting the present solid herbicidal composition with a large amount of water for use on-site, the present solid herbicidal composition becomes a low viscosity solution suitable for spraying.

Furthermore, the solid herbicidal composition according to the present invention may optionally contain, in addition to the essential paraquat and thickening agent, various conventional ingredients such as colorants, odorants, and nauseants, to further improve the safety thereof. In addition, surfactants and other herbicidal active components also can be included in the present herbicidal composition to improve the herbicidal effects and the applicability of the herbicidal composition.
The paraquat usable in the present herbicidal composition is preferably in the form of a solid. Accordingly, 1,1'-dimethyl-4,4'-dipyridyldium salts (e.g., dichloride, dibromide, and bismethylsulfate or the complex salts with, for example, manganese, iron, urea, thiourea, p-aminophenol, catechol) in the form of crystals can be directly mixed with the thickening agent. However, the industrially or commercially available paraquat solutions also can be used in the preparation of the present solid herbicidal composition by adding a water-absorbing inorganic fine powder to form an apparently water-free fluidizable solid paraquat. Any water-absorbing inorganic fine powder can be used for this purpose so long as the herbicidal effects of the paraquat and the characteristics of the thickening agents are not adversely affected. Examples of such water-absorbing inorganic fine powders are white carbon, diatomaceous earth, finely divided calcium silicate, perlite, calcined kaoline, and zeolite. These can be used alone or in any mixture thereof. There are no critical limitations to the addition amount of the water-absorbing inorganic fine powder, as long as the paraquat solution can be solidified. For example, in the case of white carbon, an equal amount of the powder can be mixed with 10 times the amount of the water contained in the aqueous paraquat solution.

There are no critical limitations to the paraquat concentration of the present solid herbicidal compositions. However, when the paraquat concentration is too low, only a small dilution ratio of the composition with water is required to obtained the desired concentration when spraying on-site and, therefore, spraying tends to become difficult from the standpoint of both the viscosity and the spraying amount, and the efficiency of the transportation and storage also tends to be decreased. On the other hand, when the paraquat concentration in the present herbicidal composition is too
high, the above-mentioned problems do not arise but the allowable safety range tends to become small from the point of view of preventing the possible occurrence of toxic or poisonous accidents.

5 For these reasons, the practically preferable concentration range of the paraquat in the present herbicidal compositions is from about 5% by weight to 40% by weight.

10 The thickening agents usable in the present invention are those which are capable of increasing the viscosity or forming the gel with the addition of a relatively small amount (e.g., 300 ml or less) of water to the solid herbicidal composition at an ambient temperature in a short period of time. There are no specific limitations to the types of the thickening agents as long as the above-mentioned requirements are fulfilled. Various natural and synthetic thickening agents can be used in the present invention. Typical examples of such thickening agents are alginic acid salts, propylene glycol alginates; carrageenan, guar gum, modified guar gum, xanthan gum, modified xanthan gum, carboxymethyl cellulose salts, methyl cellulose, hydroxyalkyl cellulose, pectine, locust bean gum, carboxymethyl starch salts, pullulan, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid salts, and polyacryl amide. These thickening agents may be used alone or in any mixture thereof. Furthermore, various conventional acids or salts also may be used in the present herbicidal compositions to further improve the gellation or thickening characteristics of the present solid herbicidal composition. The addition of inorganic salts to the present herbicidal composition can further improve the gellation properties of the present herbicidal compositions.

30 There are no definite concentrations of the thickening agents in the present herbicidal compositions since the concentrations largely depend upon the type of
thickening agent and the concentration of the paraquat component. As one practical measure, the thickening agent can be used in an amount such that the herbicidal compositions causes gellation at a paraquat component concentration of 5% by weight or more when the herbicidal composition according to the present invention is diluted with water. That is, when the paraquat concentration of the present solid herbicidal is 5% to 40% by weight, the thickening agent can be added in an amount such that all of the composition becomes a high viscous liquid or gel that cannot be easily swallowed when the present herbicidal compositions is diluted with an equal amount of water, in the case of a paraquat concentration of 5%, to 10 times the amount of water in the case of a paraquat concentration of 40%.

The solid herbicidal composition according to the present invention may further contain, as an optional component, conventional colorants, odorants, nauseants, and the like to improve the safety of the paraquat herbicide as well as surfactants and other herbicidal active components to improve the herbicidal effects. However, it should be noted that these optional components should be added in such an amount that the herbicidal effects and the other characteristics of the present composition are not adversely affected.

EXAMPLES
The present invention will be further explained by, but is by no means limited, to the following Examples and Test Examples. In the Examples, "parts" and "%" are all by weight unless otherwise specified.

Examples 1 to 7
Paraquat wettable powders were prepared by uniformly mixing and grinding solid paraquat components and other ingredients in the following formulation ratios:

(1) Paraquat dichloride 25 parts
Sodium carboxymethyl-starch 75 parts
(PRIMOJEL®: Matsutani Kagaku Kogyo
(2) Paraquat dichloride  25 parts
    Guar gum  35 parts
    (EMCO GUM® CSA 200/50: Meyhall
    Chemical A.G.)
    Borax  20 parts
    White carbon  20 parts
    (CARPLEX® #80: Shionogi & Co., Ltd.,
    "white carbon")

(3) Paraquat dichloride  15 parts
    Pullulan  60 parts
    (PULLULAN® PF30: Hayashibara
    Seibutsukagaku
    Kenkyusho K.K.)
    White carbon  20 parts
    Surfactant (Polyoxyethylene nonylphenyl
    ether)  5 parts

(4) Paraquat dichloride  15 parts
    Polyvinyl pyrrolidone  60 parts
    (Polyvinyl pyrrolidone K-90: Wako Pure
    Chemical Industries, Ltd.)
    White carbon  20 parts
    Surfactant  5 parts
    (Polyoxyethylene higher aliphatic alcohol
    ether)

(5) Paraquat dichloride  15 parts
    Carboxymethyl starch  60 parts
    (Solvitose® C-5: Matsutani Kagaku
    Kogyo Co., Ltd.)
    White carbon  20 parts

(6) Paraquat dichloride  25 parts
Xanthan gum 20 parts
(KELZAN®: Kelco Division of Merck, "Xanthan gum" hereinbelow)
White carbon 30 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)
Foaming agent
malic acid 10 parts
sodium bicarbonate 10 parts
Paraquat dimethylsulfate 30 parts
Xanthan gum 40 parts
White carbon 25 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)

Examples 8 to 21
Paraquat wettable powders were prepared by uniformly mixing and grinding a concentrated paraquat solution (i.e., aqueous solution containing 37% by weight of paraquat dichloride) and other ingredients in the following formulation ratios:

(8) Concentrated paraquat solution
27 parts
Sodium alginate 45 parts
(KELGIN®: Kelco Division of Merck)
White carbon 23 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)

(9) Concentrated paraquat solution
40 parts
Propylene glycol alginate 20 parts
(KIMIROID®: Kimitsu Kagaku Kogyo K.K)
White carbon 35 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)

(10) Concentrated paraquat solution
27 parts
- 10 -

Carrageenan 45 parts
(TAKARAGEN G50: Takagen Corporation)

White carbon 23 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)

5

Concentrated paraquat solution

Guar gum 40 parts
(EMCO GUM CSA 200/50)

White carbon 15 parts
Surfactant 35 parts
(Polyoxyethylene nonylphenyl ether)
Nauseant 5 parts

10

Concentrated paraquat solution

Odorant 1 part
(Emetine hydrochloride)

(β-Phenethyl alcohol)

15

Concentrated paraquat solution

Modified guar gum 40 parts
(JAGUAR HP-8: Meyhall Chemical AG)

White carbon 15 parts
Surfactant 35 parts
(Polyoxyethylene nonylphenyl ether)

20

Nauseant 5 parts
(Tartar emetic)

β-Phenethyl alcohol 1 part

25

Concentrated paraquat solution

Xanthan gum 40 parts
(KELZAN)

White carbon 15 parts
Surfactant 30 parts
(Polyoxyethylene nonylphenyl ether)

30

Anhydrous sodium sulfate 10 parts

35

Concentrated paraquat solution

27 parts
Sodium carboxymethyl cellulose 45 parts

(SUNROSE® SN 20TC: Sanyo
Kokusaku Pulp Co., Ltd.)

5 White carbon 23 parts
Surfactant 4 parts
(Polyoxyethylene nonylphenyl ether)

(15) Concentrated paraquat solution 50 parts

10 Methyl cellulose 10 parts
(MAPOROSE® M-10000: Matsumoto Yushi
Seiyaku K.K.)

White carbon 36 parts
Surfactant 4 parts
(Polyoxyethylene nonylphenyl ether)

(16) Concentrated paraquat solution 20 parts

Sodium carboxymethyl starch 57 parts
(PRIMOJEL®)

20 White carbon 18 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)

(17) Concentrated paraquat solution 27 parts

25 Polyvinyl alcohol 45 parts
(PVA 117S: Kuraray Co., Ltd.)
White carbon 23 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)

(18) Concentrated paraquat solution 40 parts

Polyacrylamide 24 parts
(VISCOMATE® NS: Showa Denko K.K.)
White carbon 31 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)

(19) Concentrated paraquat solution
Pectin 45 parts
(GENU PECTIN BB RAPID SET; the Copenhagen Pectin Factory Ltd.)
White carbon 23 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)
(20) Concentrated paraquat solution

Xanthan gum 14 parts
(KELZAN®)
Locust bean gum 10 parts
(MEYPRODYN®: Meyhall Chemical AG)
White carbon 31 parts
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)
(21) Concentrated paraquat solution

Xanthan gum 18 parts
(KELZAN®)
Diatomaceous earth 37 parts
(RADIOLITE: Showa Kagaku K.K.)
Surfactant 5 parts
(Polyoxyethylene nonylphenyl ether)
(25) Example 22
The following ingredients were dissolved in water.
Paraquat dichloride 30 parts
Guar gum 30 parts
(EMCO GUM® CSA 200/50)
White carbon 23 parts
(CARPLEX® #80)
Surfactant 7 parts
(Polyoxyethylene nonylphenyl ether)
Sodium sulfate 10 parts
(30) The resultant solution was granulated by a spray dryer to obtain a granular paraquat wettable powder.

Examples 23 to 25
Paraquat wettable powders having the following compositions were prepared by uniformly mixing and grinding concentrated aqueous paraquat solution and the other ingredients.

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<td>Guar gum</td>
<td>23 parts</td>
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<td>White carbon</td>
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<td>10</td>
<td>(24) Paraquat dichloride</td>
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<td>Carrageenan</td>
<td>23 parts</td>
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<td></td>
<td>White carbon</td>
<td>42 parts</td>
</tr>
<tr>
<td>15</td>
<td>(25) Paraquat dichloride</td>
<td>35 parts</td>
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<tr>
<td></td>
<td>Xanthan gum</td>
<td>23 parts</td>
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<tr>
<td></td>
<td>(KELZAN®)</td>
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<tr>
<td></td>
<td>White carbon</td>
<td>42 parts</td>
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**Test Example 1**

A 30 g amount of the solid composition prepared in Example 1 was mixed with 150 ml of water while stirring so as to obtain a mixture having a paraquat concentration of 5%. The mixture became pasty shortly after the water was added. Thus, a pasty mixture, which is difficult to be swallowed, was obtained.

The resultant pasty paraquat composition was then diluted with water in such a ratio that 50 g of the effective component was included in 150 liters of the diluted composition. The diluted herbicidal composition thus obtained was sprayed under pressure to foliage (or stems and leaves) of crabgrass, purple nutsedge, common lambsquarter, pigweed, and barnyard millet, grown in test pots, by using a pressure type atomizer in such an amount that 50 g of the active component per 10 are was applied. Prior to the spraying, a conventional nonionic type spreading agent was added to the herbicidal composition.

During the spraying, no clogging in the spray nozzle of the atomizer occurred. When the herbicidal
effects were compared with those of commercially available paraquat solution 5 days after the treatment, no substantial difference was observed.

Test Example 2

A 50 g amount of the solid composition prepared in Example 11 was mixed with 150 ml of water while stirring so as to obtain a mixture having a paraquat concentration of 5%. The mixture became pasty shortly after the water was added. Thus, a pasty mixture, which is difficult to be swallowed, was obtained.

The resultant pasty paraquat composition was then diluted with water in such a ratio that 50 g of the effective component is included in 150 liters of the diluted composition. The diluted herbicidal composition thus obtained was sprayed under pressure onto the foliage of crabgrass, purple nutsedge, common lambsquarter, pigweed, and barnyard millet grown in test pots, by using a pressure type atomizer in such an amount that 50 g of the active component per 10 are was applied.

Prior to the spraying, a conventional nonionic type spreading agent was added to the herbicidal composition. During the spraying, no clogging in the spray nozzle of the atomizer occurred. When the herbicidal effects were compared with those of a commercially available paraquat solution 5 days after the treatment, no substantial difference was observed.

Test Example 3

A 50 g amount of the solid composition prepared Example 13 was mixed with 150 ml of water while stirring so as to obtain a mixture having a paraquat concentration of 5%. The mixture became pasty shortly after the water was added. Thus, a pasty mixture, which is difficult to be swallowed, was obtained.

The resultant pasty paraquat composition was then diluted with water in such a ratio that 50 g of the effective component was included in 150 liters of the diluted composition. The diluted herbicidal composition
thus obtained was sprayed under pressure onto the foliage of crabgrass, purple nutsedge, common lambsquarter, pigweed, and barnyard millet grown in test pots, by using a pressure type atomizer in such an amount that 50 g of the active component per 10 are was applied. Prior to the spraying, a conventional nonionic type spreading agent was added to the herbicidal composition.

During the spraying, no clogging in the spray nozzle of the atomizer occurred. When the herbicidal or weeding effects were compared with those of a commercially available paraquat solution 5 days after the treatment, no substantial difference was observed.

**Test Example 4**

A 40 g amount of the solid composition prepared in Example 15 was mixed with 150 ml of water while stirring so as to obtain a mixture having a paraquat concentration of 5%. The mixture became pasty shortly after the water was added. Thus, pasty mixture, which is difficult to be swallowed, was obtained.

The resultant pasty paraquat composition was then diluted with water in such a ratio that 50 g of the effective component was included in 150 liters of the diluted composition. The diluted herbicidal composition thus obtained was sprayed under pressure onto the foliage of crabgrass, purple nutsedge, common lambsquarter, pigweed, and barnyard millet grown in test pots, by using a pressure type atomizer in such an amount that 50 g of the active component per 10 are was applied. Prior to the spraying, a conventional nonionic type spreading agent was added to the herbicidal composition.

During the spraying, no clogging in the spray nozzle of the atomizer occurred. When herbicidal effects were compared with those of a commercially available paraquat solution 5 days after the treatment, no substantial difference was observed.

**Test Example 5**

The herbicidal effects of the paraquat wettable
powders obtained in Examples 23 to 25 were evaluated in an agricultural field. As Reference Examples, a 24% aqueous paraquat solution and a 32% bialaphos liquid agent were used. The weeds used for the test were crabgrass having a height of 25 to 30 cm, smartweed having a height of 50 cm, common lambsquarter having a height of 50 cm, and pigweed having a height of 25 cm.

The area in each test was 1.5 m x 2 m (i.e., 3 m²). The diluted herbicidal composition samples containing 0.3% of a surfactant were sprayed by using a pressure type spray atomizer at an active component amount of 0.5 or 1 kg A.I. (i.e., active ingredient)/ha and at a spraying water amount of 1000 l/ha.

Six days after the spraying, the herbicidal effects were observed according to the following standard:
0 ... No effect
100 ... Complete kill

The results are as shown in Table 1. As is clear from the results shown in Table 1, since the grass height at the time of the treatment is relatively large, complete killing was not obtained at a rate of 0.5 kg A.I./ha. However, in the case of 1.0 kg A.I./ha, good results were obtained and there was no substantial difference between the compositions of Examples 23 and 25 and the conventional paraquat solution.
<table>
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<td>Crabgrass</td>
<td>Smartweed</td>
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<td>Example No. 23</td>
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<td>60</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>95</td>
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<td>85</td>
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<td>1.0</td>
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CLAIMS

1. A contradeglutitious solid herbicidal composition comprising a 1,1'-dimethyl-4,4'-dipyridylium salt and a thickening agent.

2. A herbicidal composition as claimed in claim 1, further comprising a water absorbable inorganic fine powder capable of converting an aqueous 1,1'-dimethyl-4,4'-dipyridylium solution into a solid form.

3. A herbicidal composition as claimed in claim 2, wherein said water absorbable inorganic fine powder is at least one member selected from the group consisting of white carbon, diatomaceous earth, finely divided calcium silicate, perlite, calcined kaoline, and zeolite.

4. A herbicidal composition as claimed in claim 1, wherein said thickening agent is at least one agent selected from the group consisting of alginic acid salts, propylene glycol alginites, carrageenan, guar gum, modified guar gum, xanthan gum, modified xanthan gum, carboxymethyl cellulose salts, methyl cellulose, hydroxyalkyl cellulose, pectine, locust bean gum, carboxymethyl starch salts, pullulan, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylic acid salts, and polyacryl amide.

5. A herbicidal composition as claimed in claim 1, wherein the content of the 1,1'-dimethyl-4,4'-dipyridylium salt in the composition is 5% to 40% by weight.

6. A herbicidal composition as claimed in claim 1, wherein the content of the thickening agent in the composition is such that the composition becomes substantially non-viscous upon the addition of an equal amount to 10 time the amount of water based on the composition and that the composition becomes an easily sprayable low viscosity liquid upon the addition of at least 1500 times the amount of water based on the composition.

7. A herbicidal composition as claimed in claim 1,
wherein said composition further comprises a surfactant and a nauseant.
## INTERNATIONAL SEARCH REPORT

### I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC: A 01 N 25/32; A 01 N 25/14

### II. FIELDS SEARCHED

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Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched

### III. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>EP, AI, 0174101 (MERCK &amp; CO.) 12 March 1986, see page 1, line 25 - page 2, line 28; page 4, line 4 - page 5, line 10; example 6; claims</td>
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<td>GB, A, 1395502 (I.C.I.) 29 May 1975, see page 1, line 53 - page 2, line 15; page 2, line 112 - page 3, line 22; page 3, line 75 - page 4, line 2; examples 2, 3, 7, 8, 10; claims</td>
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<td>US, A, 4046552 (G.E. DAVIES et al.) 6 September 1977, see column 4, lines 12-30; examples 3, 4; claims 1-4, 11, 13, 14</td>
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* Special categories of cited documents: 10
  "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)
  "C" document referring to an oral disclosure, use, exhibition or other means
  "M" document published prior to the international filing date but later than the priority date claimed

** "T" later document published after the international filing date on 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

"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.

*A* document member of the same patent family

### IV. CERTIFICATION

Date of the Actual Completion of the International Search: 2nd July 1986

Date of Mailing of this International Search Report: 31 JUL 1986

International Searching Authority: EUROPEAN PATENT OFFICE

Signature of Authorized Officer: M. VAN MOL

Form PCT/ISA/210 (second sheet) (January 1985)
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<td>C.C. Tanner et al., &quot;Control of submerged weeds in flowing water using viscous gel diguad&quot;, page 188, abstract no. 1898k, see the whole abstract &amp; Proc. N.Z. Weed Pest Control Conf. volume 37, 1984, pages 46-49</td>
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This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDF file on 22/07/86.

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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82.