

633678

COMMONWEALTH OF AUSTRALIA

Case: 39-21(2838)A AS

Patents Act 1952

Form 1

Regulation 9

APPLICATION FOR A STANDARD PATENT OR
A STANDARD PATENT OF ADDITION

We, MONSANTO COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, having its principal place of business at 800 North Lindbergh Boulevard, St. Louis, State of Missouri, United States of America, hereby apply for the grant of a Standard Patent for an invention entitled:

"PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE"

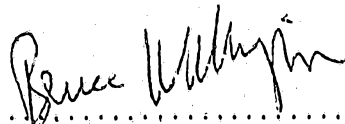
which is described in the accompanying complete specification.

This application is a Convention application and is based on an application numbered 543,016 for a patent or similar protection made in United States of America on 25th June 1990.

Our address for service is care of E.F. WELLINGTON & CO., Patent and Trade Mark Attorneys, 312 St. Kilda Road, Melbourne, in the State of Victoria, Commonwealth of Australia.

DATED this 24th day of January, 1991

For and on behalf of
MONSANTO COMPANY,



.....
BRUCE S. WELLINGTON
Patent Attorney for Applicant Company

To: The Commissioner of Patents,
Commonwealth of Australia.

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

FORM 8

REGULATION 12(2)

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION
~~XXXXXXXXXXXX~~ FOR A PATENT OR PATENT OF ADDITION.

In support of the Convention Application made ~~XXXXXXXXXXXXXXXXXXXXXXXXXXXX~~
~~XXX~~ by MONSANTO COMPANY for a patent for an invention entitled:

PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

I, William Harry Duffey, General Patent Counsel, Monsanto Company, of 800 North Lindbergh Boulevard, St. Louis, 63167, in the State of Missouri, United States of America, do solemnly and sincerely declare as follows:

1. I am authorized by MONSANTO COMPANY, the applicant for the Patent to make this declaration on its behalf.

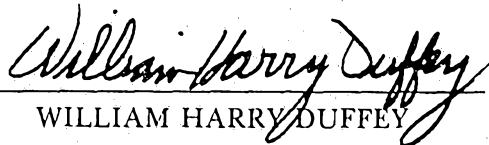
2. The basic application as defined by Section 141 of the Act was made at the Patent Office, Washington, District of Columbia, in the United States of America on the 25th of June 1990, by DONALD LEE FIELDS, JR.

3. DONALD LEE FIELDS, JR., of
406 Stephanie Lane,
Manchester, Missouri 63011,
United States of America,

is ~~XXX~~ the actual inventor(X) of the invention, and the facts upon which the MONSANTO COMPANY is entitled to make the application are as follows:
The Company is the assignee of the actual inventor(X).

4. The basic application referred to in paragraph 2 of this declaration was the first application made in a Convention country in respect of the invention, the subject of the application.

DECLARED at St. Louis, Missouri, aforesaid this 6th day of December 90, 1990.


WILLIAM HARRY DUFFEY

To Commissioner of Patents
COMMONWEALTH OF AUSTRALIA



AU9169933

(12) PATENT ABRIDGMENT (11) Document No. AU-B-69933/91
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 633678

(54) Title
PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

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543016	25.06.90	US UNITED STATES OF AMERICA

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(71) Applicant(s)
MONSANTO COMPANY

(72) Inventor(s)
DONALD LEE FIELDS JR.

(74) Attorney or Agent
E F WELLINGTON & CO , 312 St Kilda Road, MELBOURNE VIC 3004

(57) Claim

1. A process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide and converting the intermediate to N-phosphonomethylglycine, characterized by contacting N-phosphonomethyliminodiacetic acid with a substantially stoichiometric amount of peroxide in the presence of an amount of a catalyst selected from the group consisting of a water-soluble tungsten compound, and a mixture of a water-soluble tungsten compound and a water-soluble molybdenum compound, effective to form N-phosphonomethyliminodiacetic acid-N-oxide, and thereafter converting the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

5. The process of Claim 4 wherein the tungsten compound is an alkali metal tungstate and the molybdenum compound is an alkali metal molybdate or ammonium molybdate.

8. The process of Claim 7 wherein the weight ratio of tungsten compound to molybdenum compound is from 40:60 to 60:40.

633678

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

FORM 10

Case: 39-21(2838)A A

Application Number:
Lodged:

Class: Int. Class

Complete specification: Lodged:
Accepted:
Published:

Priority:

Related Art:

Name of Applicant: MONSANTO COMPANY

Address of Applicant: 800 North Lindbergh Boulevard,
St. Louis Missouri, 63167,
United States of America.

Actual Inventor/s: DONALD LEE FIELDS, JR.

Address for Service: E.F. WELLINGTON & CO.,
Patent and Trade Mark Attorneys,
312 St. Kilda Road,
Melbourne, 3004, Victoria.

Complete Specification for the invention entitled:

"PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE"

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

Background of the Invention

This invention relates to a process for the preparation of N-phosphonomethylglycine, and more particularly to the preparation of N-phosphonomethyl-
5 iminodiacetic acid-N-oxide from N-phosphonomethylimino-
diacetic acid using peroxides, which is converted to N-phosphonomethylglycine.

N-Phosphonomethylglycine, known also by its common name glyphosate, is a highly effective, commercially important, phytotoxicant useful in controlling
10 a large variety of weeds. It is applied to the foliage of a very broad spectrum of annual and perenial grasses and broadleaf plants. Industrial uses include control of weeds along roadsides, water-
15 ways, transmission lines, in storage areas, and in other nonagricultural areas. Usually, N-phosphonomethylglycine is formulated into herbicidal compositions in the form of its various salts in solution, preferably water.

20 U.S. Patent 3,950,402 to Franz discloses a process for the production of N-phosphonomethylglycine by forming an admixture of N-phosphonomethylimino-
diacetic acid, water, and a metallic catalyst selected from the noble metals, heating the admixture to an
25 elevated temperature (greater than 70°C to avoid low yields) and contacting the admixture with a free oxygen-containing gas.

30 U.S. Patent 3,954,848 to Franz discloses a process for the production of N-phosphonomethylglycine by reacting N-phosphonomethyliminodiacetic acid with an oxidizing agent, such as hydrogen peroxide, in an aqueous acidic medium in the presence of a strong acid at a temperature of from about 70°C to about 100°C. It is disclosed that one should employ at least 2

moles of the hydrogen peroxide for each mole of the N-phosphonomethyliminodiacetic acid, and preferably more.

5 Hungarian Patent Application No. 187,347 discloses a process for the preparation of N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with peroxides using a catalytic amount of a metal compound selected from compounds of silver, iron, tin, lead, manganese or molybdenum. Molybdates are preferred. At temperatures lower than 80°C, usually a contaminated end product is obtained. Typically, the reaction is carried out at a temperature of above 80°C and preferably above 100°C at pressures exceeding atmospheric, wherein the intermediate N-oxide is decomposed as rapidly as it forms. It is further disclosed that at least two mole equivalents of peroxide should be used for each mole equivalent of N-phosphonomethyliminodiacetic acid.

20 A publication entitled "Peroxygen Compounds in Organic Synthesis" published by Interox as a technical bulletin discloses that transition metal compounds, like sodium tungstate or molybdate or the relevant oxides, promote oxidation reactions by a non-radical mechanism. Peroxidic complexes also play a transient role in the metal catalyzed oxidation of olefins and acetylenes by alkyl hydroperoxides.

30 Although satisfactory results are obtained by the above processes to make N-phosphonomethylglycine, all of them suffer from one or more disadvantages, such as the use of excessive amounts of peroxide, and/or reaction at elevated temperatures and pressures. Now, there is disclosed a process which provides N-phosphonomethylglycine in high yields at 35 modest temperatures and at atmospheric pressure using

substantially stoichiometric amounts of peroxide to oxidize the N-phosphonomethyliminodiacetic acid to the desired N-phosphonomethylglycine.

Summary of the Invention

5 These and other advantages are achieved in a process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide and converting the intermediate to
10 N-phosphonomethylglycine, the improvement which comprises contacting N-phosphonomethyliminodiacetic acid with a peroxide in the presence of an effective amount of a catalyst selected from the group consist-
15 ing of water-soluble tungsten compounds and a mixture of a water-soluble tungsten compound and a water-soluble molybdenum compound to form N-phosphonomethyl-
iminodiacetic acid-N-oxide, and thereafter converting the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

Detailed Description of the Invention

20 The N-phosphonomethyliminodiacetic acid starting material can be prepared by methods known to those skilled in the art. For example, this material can be produced by the reaction of formaldehyde,
25 iminodiacetic acid and orthophosphorous acid in the presence of sulfuric acid. Although the N-phosphonomethyliminodiacetic acid mixture resulting from this reaction can be employed directly in the process of this invention, it is preferred to isolate the N-phos-
30 phonomethyliminodiacetic acid and then employ it herein.

 Any number of peroxides known to those skilled in the art can be used to prepare the N-phosphonomethyliminodiacetic acid-N-oxide. Suitable per-
35 oxides include hydrogen peroxide, performic acid, peracetic acid, perbenzoic acid, peroxytrifluoro-

acetic acid, benzoyl peroxide, benzenepersulfonic acid, and the like. Hydrogen peroxide is preferred, and it is advantageous to use hydrogen peroxide in the form of a concentrated solution, say
5 between about 30% and 60%.

In the process of the present invention, the N-phosphonomethyliminodiacetic acid-N-oxide is prepared by contacting N-phosphonomethyliminodiacetic acid with a peroxide in the presence of a catalytic
10 amount of a water-soluble tungsten compound or a mixture of a water-soluble tungsten compound and a water-soluble molybdenum compound. Mixtures of a water-soluble tungsten compound and a water-soluble molybdenum compound are preferred.

The temperature of the process to prepare the N-phosphonomethyliminodiacetic acid-N-oxide can vary from as low as about 20°C to about 70°C. Although temperatures below about 20°C can be used, such temperatures would require the use of cooling,
15 and no advantages are obtained. At temperatures above about 70°C, degradation of the N-phosphonomethyliminodiacetic acid-N-oxide is observed, which affects the final yield of the desired N-phosphonomethylglycine. Temperatures between about 20°C and
20 about 65°C are preferred.

The salts of tungsten useful as catalysts to oxidize the N-phosphonomethyliminodiacetic acid to the N-phosphonomethyliminodiacetic acid-N-oxide are known to those skilled in the art. It is only necessary that the tungsten salts are soluble in the re-
25 action medium. Suitable tungsten compounds include tungstic acid, 1,2-tungstophosphate, and barium tungstate. The alkali metal tungstates, such as sodium tungstate, potassium tungstate, and the like,
30 provide satisfactory results, and the alkali metal tungstates are preferred.

The salts of molybdenum useful in admixture with a water-soluble tungsten compound as catalysts to oxidize the N-phosphonomethyliminodiacetic acid to the N-phosphonomethyliminodiacetic acid-N-oxide are also known to those skilled in the art. It is only necessary that the molybdenum salts are soluble in the reaction medium. Suitable molybdenum compounds include molybdenum halides, such as molybdenyl tri-chloride and the like, alkali metal molybdates, such as sodium molybdate and the like, or more complex salts, such as the ammonium or alkali metal dimolybdates. Sodium and ammonium molybdates are preferred.

The amount of catalyst to convert the N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide can vary within wide limits. Concentrations between about 0.005 and about 5 wt.% catalyst, based on the weight of the N-phosphonomethyliminodiacetic acid, provide satisfactory results. At concentrations of less than about 0.005 wt.% catalyst, the reaction is slow, and at concentrations greater than about 5 wt.%, no particular advantage is seen, although such higher concentrations are not harmful. It is preferred to use between about 0.01 wt.% and about 1 wt.% based on the weight of the N-phosphonomethyliminodiacetic acid.

When a mixture of a water-soluble tungsten compound and a water-soluble molybdenum compound is used to form the N-phosphonomethyliminodiacetic acid-N-oxide, the ratio of the tungsten compound to the molybdenum compound can vary within wide limits. Satisfactory results have been obtained when the ratio of the tungsten compound to the molybdenum compound varies from about 90:10 to 10:90. However, it is preferred to use a weight ratio of the tungsten compound to the molybdenum compound between about 25:75 and 75:25, and even more preferred to use a weight ratio of tungsten compound to molybdenum compound between about 60:40 and 40:60.

In the process of the present invention, the amount of peroxide should be the stoichiometric amount required to convert the N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide. As will occur to those skilled in the art, when less than the stoichiometric amount of peroxide is used, the yield of the desired N-phosphonomethylglycine is lower. A slight excess of peroxide can be used to insure a quantitative conversion of the N-phosphonomethyliminodiacetic acid to the intermediate, but there is no advantage to using large excesses of peroxide, and excesses of peroxide may be deleterious if water-soluble compounds, such as ferrous sulfate, ferrous halide or an alkali metal metabisulfite compound, is used to convert the intermediate to N-phosphonomethylglycine.

The N-phosphonomethyliminodiacetic acid-N-oxide intermediate is contacted with a catalytic amount of a substance selected from the group consisting of iron metal, the water-soluble salts of a vanadium compound, a ferrous salt, or a mixture of a water-soluble sulfide, sulfite, or bisulfite compound and a water-soluble molybdate compound to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine. Suitable vanadium compounds that are soluble in the reaction mixture include vanadium pentoxide, vanadium sulfate, vanadium chloride and the like. Suitable water-soluble ferrous compounds that can be used in the process of the present invention include ferrous sulfate and ferrous halides, such as ferrous chloride, ferrous bromide and the like. In addition, a sulfide, sulfite or metabisulfite compound, such as sodium sulfide, sodium sulfite, sodium metabisulfite, potassium metabisulfite or ammonium metabisulfite, can be used in a mixture with a water-soluble molybdenum

compound, such as molybdenum trichloride, sodium molybdate, ammonium molybdate and the like, to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine.

5 The amount of catalyst to convert the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine depends upon the catalyst used and the amount of peroxide in excess of that required to produce the intermediate from the N-phosphonomethyl-
10 iminodiacetic acid. When iron metal is used, the rate of reaction to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine depends upon the surface area of the iron metal present, and it is preferred to use from about 1
15 wt.% to about 10 wt.% of the metal, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide present. In addition, it is preferred to use the iron metal in any form that provides a high surface area, for example, a wool, a powder or finely
20 divided granules.

 When a water-soluble compound is used as a catalyst to convert the intermediate to N-phosphonomethylglycine, the excess peroxide will react with the water-soluble compound, and in addition to the amount
25 of compound required to react with the excess peroxide, there should also be a sufficient amount of the water-soluble compound to catalyze the reaction of the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine. The amount of water-soluble compound remaining after reaction with the peroxide to
30 act as a catalyst should be at least 0.01 wt.%, based on the amount of the N-phosphonomethyliminodiacetic acid-N-oxide. Excess water-soluble compound as high as 10%, even higher, can be used, but there does not
35 seem to be an advantage to using such higher concentrations for the conversion of the intermediate to N-phosphonomethylglycine, although such higher concentrations are not harmful. It is preferred to use

between about 0.01 wt.% and about 1 wt.% of the water-soluble compound, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide, after reaction with any excess peroxides.

5 The temperature required to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine can vary within wide limits. It is preferred to add the catalyst at or near room temperature (about 20°C)
10 because vigorous gas evolution frequently occurs, and the conversion of N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine is exothermic. It is preferred to keep the reaction temperature below about 80°C by cooling the reaction vessel or using a
15 low catalyst charge. Temperatures above about 80°C will provide N-phosphonomethylglycine, but some yield loss may occur.

 The concentration of the N-phosphonomethyliminodiacetic acid as the starting material can vary
20 within wide limits in the process of the present invention. For example, an aqueous suspension containing up to 50 wt.% N-phosphonomethyliminodiacetic acid can be used. Higher concentrations of the N-phosphonomethyliminodiacetic acid can be used, but it can
25 present processing difficulties because of the thickness of the slurry. On the other hand, an aqueous solution of the N-phosphonomethyliminodiacetic acid containing about 5 wt.% of the N-phosphonomethyliminodiacetic acid can also be used. Lower concentrations
30 can also be used, but it requires processing large volumes of liquid in the process of the present invention. It is preferred to use an aqueous slurry containing from about 20 wt.% to about 40 wt.% of the N-phosphonomethyliminodiacetic acid.

35 This invention is further illustrated by, but not limited to, the following examples. Conversion is calculated by dividing the moles of other

compounds produced by the moles of starting N-phosphonomethyliminodiacetic acid and multiplying by 100. Selectivity is calculated by dividing the moles of N-phosphonomethylglycine produced by the moles of N-phosphonomethyliminodiacetic acid converted and multiplying by 100.

Example 1

This Example illustrates the process of the present invention using a water-soluble tungsten salt to convert N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide, and the subsequent formation of N-phosphonomethylglycine.

(A) To a 100 ml round bottomed flask was added water (25 ml), N-phosphonomethyliminodiacetic acid (20 g), 47% hydrogen peroxide (7.1 g) and sodium tungstate (0.05 g). The mixture was heated to 65°C and maintained at this temperature until a solution was obtained (about 58 minutes), indicating the N-oxide was formed. The solution was then allowed to cool to about 55°C and stirred for an additional 30 minutes.

(B) After cooling to room temperature, vanadyl sulfate (0.05 g, 29% H₂O) was added to the solution. After stirring for about 5 minutes, the color of the solution changed from blue to light green. Gas evolution began with a slow exotherm. When the temperature reached about 40°C, the exotherm greatly accelerated to 65°C and cooling water was applied to maintain the solution at this temperature. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 96.7%, and the selectivity to N-phosphonomethylglycine was 91.4%.

Example 2

This Example illustrates the process of the present invention using a mixture of a water-soluble tungsten salt and a water-soluble molybdenum salt to convert N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide, and the subsequent formation of N-phosphonomethylglycine.

(A) To a 100 ml round bottomed flask was added water (25 ml), N-phosphonomethyliminodiacetic acid (20 g), 47% hydrogen peroxide (7.1 g), sodium tungstate (0.05 g) and sodium molybdate (0.05 g). The mixture was heated to 65°C and maintained at this temperature until a solution was obtained (about 52 minutes), indicating that the N-oxide was formed. The solution was then allowed to cool to about 55°C and stirred for an additional 1 hour and 45 minutes.

(B) After cooling to room temperature, sodium metabisulfite (0.45 g) was added to the solution. After stirring for about 5 minutes, gas evolution was observed with a slow exotherm. When the temperature reached about 40°C, the exotherm greatly accelerated to 65°C and cooling water was applied to maintain the solution at this temperature. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrates and the solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 91.8%, and the selectivity to N-phosphonomethylglycine was 96.3%.

Although the invention has been described in terms of specified embodiments which are set forth in considerable detail, it should be understood that this is by way of illustration only, and that alternative embodiments and operating techniques will become apparent to those skilled in the art in view of the disclosure. Accordingly, modifications can be

made without departing from the spirit of the described invention, as defined in the following claims.

5 The matter contained in each of the following claims is to be read as part of the general description of the present invention.

The claims defining the invention are as follows:

1. A process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide and converting the intermediate to N-phosphonomethylglycine, characterized by contacting N-phosphonomethyliminodiacetic acid with a substantially stoichiometric amount of peroxide in the presence of an amount of a catalyst selected from the group consisting of a water-soluble tungsten compound, and a mixture of a water-soluble tungsten compound and a water-soluble molybdenum compound, effective to form N-phosphonomethyliminodiacetic acid-N-oxide, and thereafter converting the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

2. The process of Claim 1 wherein the amount of catalyst is between 0.005 wt.% and 5 wt.%, based on the weight of the N-phosphonomethyliminodiacetic acid.

3. The process of Claim 2 wherein the amount of catalyst is between 0.01 wt.% and 1 wt.%.

4. The process of any one of Claims 1 to 3 wherein the catalyst is a mixture of a water-soluble tungsten compound and a water-soluble molybdenum compound.

5. The process of Claim 4 wherein the tungsten compound is an alkali metal tungstate and the molybdenum compound is an alkali metal molybdate or ammonium molybdate.

6. The process of Claim 4 or 5 wherein the weight ratio of tungsten compound to molybdenum compound is from 10:90 to 90:10.



7. The process of Claim 6 wherein the weight ratio of tungsten compound to molybdenum compound is from 25:75 to 75:25.

8. The process of Claim 7 wherein the weight ratio of tungsten compound to molybdenum compound is from 40:60 to 60:40.

5 9. The process of any one of Claims 1 to 3 wherein the catalyst is a water-soluble tungsten compound.

10. The process of Claim 9 wherein the tungsten compound is selected from the group consisting of the alkali metal tungstates.

10 11. The process of Claim 10 wherein the tungsten compound is sodium tungstate.

12. The process of any one of Claims 1 to 11 wherein the peroxide is hydrogen peroxide.

15 13. The process of any one of Claims 1 to 12 wherein the temperature to form the N-phosphonomethyliminodiacetic acid-N-oxide is between 20°C and 70°C.

14. The process for producing N-phosphonomethylglycine as defined in Claim 1, substantially as hereinbefore described.

20 15. N-phosphonomethylglycine when obtained by the process of any one of Claims 1 to 14.

DATED this 6th day of November, 1992

MONSANTO COMPANY,
By its Patent Attorneys,
E. F. WELLINGTON & CO.,
By:

(B. S. Wellington)

A/RR/1555/8

