

1

3,146,087

**PROCESS FOR PREPARING A FERTILIZER CONTAINING WATER-INSOLUBLE NITROGEN FROM AMMONIA AND WOOD**

**Robert L. Formaini, Petersburg, and Delbert P. Schutz, Hopewell, Va., assignors to Allied Chemical Corporation, New York, N.Y., a corporation of New York**  
 No Drawing. Filed Jan. 29, 1962, Ser. No. 169,617  
 4 Claims. (Cl. 71-23)

This invention relates to a process for preparing a fertilizer containing water-insoluble nitrogen of high agronomic value. More particularly, it relates to a process for preparing such fertilizer from finely divided cellulosic materials by oxidation and ammoniation.

Numerous processes have been developed for making useful products from waste cellulosic material such as sawdust. Processes in which the cellulosic material is oxidized such as is that described in U.S. Patent 2,232,990 lead to the production of oxy cellulose which is suitable for the production of transparent films or sheets. Other processes such as the one described in British Patent 347,641 can be used to convert sawdust into fertilizer. This latter is accomplished by the simultaneous oxidation and ammoniation of the cellulosic material.

While this latter process has considerable merit in that it can lead to fertilizer products containing 10 to 20 percent nitrogen, the process is slow (lengthy reaction time), hazardous from an explosion view point and leads to products which have been found to unsatisfactory in view of their uncertain activity characteristics in use.

It is therefore an object of this invention to provide a process for converting cellulose to fertilizer which is more rapid than the processes of the prior art.

A further object is to provide a less hazardous process which is readily susceptible to control.

A still further object is to provide a process of the aforementioned type which will lead to the formation of a product having superior agronomic value, one having a total nitrogen content of about 19 to 27 percent with a water-insoluble nitrogen content of about 30 to 50 percent of the total nitrogen and relatively high activity when used in soil. For purposes of this invention relatively high activity means that the product, when applied to soil at a rate of 400 pounds of nitrogen per acre, has a nitrification rate of at least about 15 percent, preferably about 50 percent of the total nitrogen in three weeks.

It has been found that these and other objects of this invention can be attained by oxidizing finely divided cellulosic material with nitrogen dioxide at temperatures of about 20 to 120° C. until the carboxylic acid content is brought to at least about 5 percent by weight and subsequently treating the oxidized product with ammonia at pressures of at least 700 p.s.i.g. and temperatures between about 175° and about 265° C.

The first step of the process, which involves oxidation of finely divided cellulosic material with nitrogen dioxide, is carried out at 20-120° C., preferably at 20-60° C., for a period of time sufficient to incorporate appreciable quantities (say 10-15 percent) of carboxylic groups into the wood structure. It is important to use finely divided cellulosic material, such as sawdust, wood flour, or chips having thickness of about 0.01-0.02 inch, in order to speed the reaction. A 2-20 hour reaction period is generally sufficient. In defining the process, nitrogen dioxide refers to the equilibrium mixture of nitrogen dioxide (NO<sub>2</sub>) and its dimer, nitrogen tetroxide (N<sub>2</sub>O<sub>4</sub>).

The extent of oxidation of the wood is relatively uniform for a given set of oxidation conditions; however, the oxidation should be followed, at least in initial operations, by analysis of the carboxyl group content of the oxidized

2

wood. The carboxyl group content of the oxidized wood may be estimated as follows: To 0.5 g. samples of the oxidized material is added 50 cc. of distilled water and 30 cc. of 0.5 N calcium acetate solution. After standing at room temperature for two hours with frequent shaking, 30 cc. portions of the liquid are titrated with 0.1 N sodium hydroxide, using phenolphthalein indicator. The carboxyl contents are calculated as follows:

$$\frac{\text{cc. of 0.1 N NaOH} \times 0.0045 \times 100 \times 8}{\text{Wt. Sample} \times 3}$$

=percent COOH (by weight)

Operation of the wood oxidation step is simple. Wood chips or sawdust are placed in a reactor, preferably agitated. The reaction temperature is controlled by indirect cooling. Gaseous nitrogen dioxide is normally fed over a period of 2-20 hours at about atmospheric pressure to the bottom of the reactor, and during the course of the reaction, water, vapor and nitric oxide form and are displaced upward and out of the reactor. If desired, liquid N<sub>2</sub>O<sub>4</sub> may be vaporized within the reactor to furnish gaseous nitrogen dioxide.

The step of treating the oxidized wood with ammonia must be carefully controlled for depending upon conditions ammonia and oxidized wood react to form products in which the nitrogen is either soluble or insoluble by AOAC tests. (AOAC Official Methods of Analysis, Eighth Edition, 1955, page 14.) Under most known conditions, the water-insoluble products are resious and the activity of the nitrogen is low as determined by soil nitrification tests. The production of solid ammonia-wood reaction products in which a high percentage of nitrogen is insoluble, and this insoluble nitrogen has a high degree of activity requires, therefore, careful maintenance of particular conditions.

Control of both reaction temperature and pressure are important and should be correlated to produce a desirable water-insoluble fertilizer i.e., a fertilizer containing a large proportion of water-insoluble nitrogen which is active as determined by nitrification tests in soil. Normally, the ammonia pressure over the oxidized wood should be maintained at least at 700 p.s.i.g., preferably at about 1500-3000 p.s.i.g. Use of pressure below about 700 p.s.i.g. lowers the amount of bound nitrogen to uneconomic levels, whereas reaction pressures much above 3000 p.s.i.g. involve much higher equipment cost. The control of temperature appears to be a more important factor relative to the activity of the water-insoluble nitrogen in the product.

Temperature control is considered more critical than pressure control in the ammoniation step. At the high superatmospheric pressures specified for the process, reaction temperatures below about 175° C. tend to produce a product low in total nitrogen. A desirable fertilizer containing 19-27 percent or more total nitrogen, a large portion of which is active and water-insoluble, is produced in the range 175-265° C. At reaction temperatures above 265° C., the material produced is high in water-insoluble nitrogen, but this product is largely inactive and unavailable to plants within a normal growing season. Best results have been obtained using reaction temperatures in the range 185-230° C., and this range is preferred.

The reaction time for the ammoniation step will vary with the reaction temperature. At 175-265° C. the reaction is essentially complete in 0.5-4 hours. Higher temperatures tend to speed the reaction, but as indicated above, the reaction temperature must be limited to below 265° to avoid formation of inactive nitrogen.

In the following examples quantities of material are given in parts by weight.

## Example I

200 parts of hardwood flour was weighed into a rotating reaction vessel. A total of 475 parts of gaseous nitrogen dioxide at 30 to 35° C. was passed into the vessel along the central axis over the tumbling mass for a period of 3.5 hours. The off-gases escaped from the oxidation chamber by way of an annular opening along the inlet nitrogen dioxide tube. The reaction vessel was maintained at about 20° C. during the nitrogen dioxide addition. After the nitrogen dioxide flow was stopped, air was passed over the oxidized material to remove excess nitrogen oxides. The carboxylic acid content of the wood had been brought by the treatment to about 10 percent by weight as measured by titration with sodium hydroxide.

A total of 25 parts of the oxidized wood was weighed into a stainless steel autoclave. The autoclave was then chilled, evacuated, and 54 parts anhydrous NH<sub>3</sub> was added. The autoclave was heated to about 205° C. for one hour. The autogenous pressure reached approximately 2250 p.s.i.g. After the one-hour reaction period, the autoclave was cooled, the excess NH<sub>3</sub> bled off, and the ammoniated solids dried in a vacuum oven at 60° C. to constant weight. An 80 percent overall yield of dried solids (based on wt. percent of untreated wood) was realized.

The dried solids contained 19.7 percent total nitrogen and 9.3 percent water-insoluble nitrogen by AOAC test given in "AOAC Official Methods of Analysis" (Eighth Edition, 1955), page 14. When applied to soil at a rate equivalent to 400 pounds nitrogen/acre, the ammoniated product was 51 percent nitrified in three weeks. In concurrent tests, a sample of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> was 94 percent nitrified by the soil while a sample of a commercial urea-form-type fertilizer showed 40 percent nitrification in the three-week period.

## Example II

This example was carried out in the same manner as Example I except that the temperature of the ammoniation reaction was raised to 265° C. Maximum reaction pressure was 3050 p.s.i.g. The product contained 22.0 percent total nitrogen and 18.4 percent water-insoluble nitrogen by AOAC tests. When applied to soil at a rate equivalent to 400 pounds nitrogen/acre, the ammoniated product was 14.5 percent nitrified in three weeks. This rate of nitrification is considered marginal for a commercial fertilizer.

## Control "A"

This example demonstrates that ammoniation of oxidized wood at atmospheric pressure gives a product relatively low in nitrogen content.

(a) *Oxidation step*.—Approximately 443 parts by weight of NO<sub>2</sub> vapor was passed through a bed of 435 parts of hardwood chips over a period of twenty hours at a rate of 22 parts of NO<sub>2</sub> per hour. Reaction temperature was controlled at 30–60° C. by external cooling. Samples of the oxidized wood chips were removed at intervals during the reaction period and analyzed to show the extent of oxidation. Analytical results follow.

Reaction time, hours:	Weight percent carboxyl (COOH)
1	2.6
2	4.3
3	6.3
20	14.0

After twenty hours of reaction the oxidized wood chips were removed from the bed and dried at 105° C. Approximately 392 parts of dry oxidized wood was obtained.

(b) *Ammoniation step*.—A total of 40 parts of the oxidized wood from Step (a) was heated at 260° C. in a tubular reactor and 82 parts of gaseous NH<sub>3</sub> was

passed through the tubular reactor over a period of 2.5 hours at a rate of about 33 parts of NH<sub>3</sub> per hour. A total of 26 parts of solid product was obtained. The product contained only 13 percent nitrogen by AOAC test; this nitrogen content is considered too low for use of the material as a commercial fertilizer.

## Control "B"

This example demonstrates that a reaction temperature of 270° gives a product that is relatively inactive in soil tests.

(a) *Oxidation step*.—Approximately 60 parts of hardwood chips was placed in a tubular reactor and 320 parts of NO<sub>2</sub> vapor was passed through the bed in a period of eight hours at a rate of about 40 parts per hour. A reaction temperature of 30–40° C. was maintained in the reactor tube. A total of 78 parts of oxidized wood was recovered.

(b) *Ammoniation step*.—Approximately 25 parts of the oxidized wood from Step (a) was treated with 47 parts of NH<sub>3</sub> in an autoclave at 270° C. for two hours. Pressure was 2000–3000 p.s.i.g. After two hours reaction the mixture was cooled to room temperature and the product was removed from the autoclave and dried at 60° C. About 16.7 parts of product was obtained containing 22.3 percent total nitrogen and 19 percent water-insoluble nitrogen by AOAC tests. The product did not nitrify in the soil at a sufficiently rapid rate to be a good fertilizer, i.e., the product was only 18 percent nitrified after six weeks in the soil.

Although certain preferred embodiments of the invention have been disclosed for purpose of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

We claim:

1. The process for the preparation of a fertilizer of high agronomic value having a total nitrogen content of about 19–27 percent with a water-insoluble nitrogen content of about 30 to 50 percent of the total nitrogen and nitrification rate of at least about 15 percent in three weeks in the soil, which comprises oxidizing finely divided cellulosic materials with nitrogen dioxide at temperatures of about 20–120° C. until the carboxylic acid content is brought to at least about 5 percent by weight and subsequently treating the oxidized product with ammonia at pressures of at least 700 p.s.i.g. and temperatures between about 175° and about 265° C.

2. The process for the preparation of a fertilizer of high agronomic value having a total nitrogen content of about 19–27 percent with a water-insoluble nitrogen content of about 30 to 50 percent of the total nitrogen and relatively high activity when used in soil, which comprises oxidizing finely divided cellulosic materials with nitrogen dioxide at temperatures of about 20–60° C. until the carboxylic acid content is increased to about 10 percent by weight and subsequently treating the oxidized product with ammonia at pressures about 1500–3000 p.s.i.g. and temperatures between about 185° and about 230° C.

3. The process of claim 1 in which the finely divided cellulosic material is sawdust.

4. The process of claim 1 in which the finely divided cellulosic material is wood chip, having a thickness of about 0.01–0.02 inch.

## References Cited in the file of this patent

## UNITED STATES PATENTS

2,092,100      Waynick      Sept. 7, 1937

## FOREIGN PATENTS

347,641      Great Britain      Apr. 29, 1931

361,890      Great Britain      Nov. 23, 1931

602,006      Great Britain      May 18, 1948