

## UNITED STATES PATENT OFFICE

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## PREPARATION OF CYCLO-TRIMETHYLENETRINITRAMINE

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This invention relates to the nitration of hexamethylenetetramine to cyclo-trimethylenetrinitramine, commonly called "Hexogen" or "Cyclonite."

It is well known that hexamethylenetetramine can be nitrated to cyclo-trimethylenetrinitramine by means of concentrated nitric acid. However, the best yields obtainable to date, so far as I am aware, are in the neighborhood of 70% of theory.

It is an object of my invention to prepare cyclo-trimethylenetrinitramine from hexamethylenetetramine in substantially greater yields; another object is to provide a process of nitration of hexamethylenetetramine to cyclo-trimethylenetrinitramine which may be carried out at higher and more practicable temperatures than those found necessary for the best yields to date; and, a further object is to provide a process for the nitration of hexamethylenetetramine in which the tendency for spontaneous decomposition is greatly reduced. Other and further objects will become apparent upon a perusal of this specification.

I have discovered that the addition of ammonium salts such as  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  to concentrated  $\text{HNO}_3$  produces a nitrating mixture which is particularly well adapted to the nitration of hexamethylenetetramine. The most significant effects of this addition are an important improvement in the yield of cyclo-trimethylenetrinitramine obtained from a given weight of hexamethylenetetramine and an increase in the safety of the nitration. Thus, I have found that if hexamethylenetetramine is added to, say 98%  $\text{HNO}_3$  and the reaction mixture handled under well known conditions, which give a yield of cyclo-trimethylenetrinitramine of say, 65-70% of theory, the addition of certain ammonium salts to this identical 98%  $\text{HNO}_3$  will produce a nitration mixture, which, when used in the same manner as the original 98%  $\text{HNO}_3$  will give a yield of cyclo-trimethylenetrinitramine of over 90% of theory.

In order more clearly to point out my invention, the following examples in which all parts are by weight, are given.

## Example #1

70 parts of hexamethylenetetramine were added to a mixture consisting of 875 parts of 98%  $\text{HNO}_3$  and 50 parts of ammonium nitrate, at 7° C. to 22° C., with stirring, over a period of about 45 minutes. After the addition of the

hexamethylenetetramine, the mixture was stirred for about 5 minutes, and drowned in about 3000 parts of ice and water. The precipitated cyclo-trimethylenetrinitramine was filtered off, washed with cold water, then with hot water, dried and weighed. The yield was more than 80% of theory.

Using the same nitric acid without the addition of the ammonium nitrate the yield was about 65% of theory.

## Example #2

70 parts of hexamethylenetetramine were added to 875 parts of 98%  $\text{HNO}_3$  containing 25 parts of  $\text{NH}_4\text{NO}_3$ , with stirring, at 3° C. to 10° C. The period of addition was 55 minutes and the additional stirring lasted for 15 minutes. The reaction mixture was drowned and handled in the manner described in Example 1. The yield of cyclo-trimethylenetrinitramine obtained was 94 parts or about 85% of theory. The proportion of the hexamethylenetetramine to  $\text{NH}_4\text{NO}_3$  in this example is one to 0.36, or about 8 to 3.

## Example #3

Using 75 parts of ammonium nitrate in place of the 25 parts of the previous example, the yield of cyclo-trimethylenetrinitramine obtained was about 70% of theory indicating that the proportion of  $\text{NH}_4\text{NO}_3$  to  $\text{HNO}_3$  is on the verge of being too high from the standpoint of improving the yield of hexogen, but is a distinct advantage from the standpoint of safety of nitration and ease of drowning. This amount of  $\text{NH}_4\text{NO}_3$  is equivalent to 16 parts  $\text{NH}_3$  for 858 parts of 100%  $\text{HNO}_3$  or about 1 part  $\text{NH}_3$  per 54 of 100%  $\text{HNO}_3$ .

## Example #4

Using 100 parts of ammonium nitrate in place of the 25 parts of the previous example, the yield of cyclo-trimethylenetrinitramine obtained was only 60% of theory, indicating that this proportion of  $\text{NH}_4\text{NO}_3$  to  $\text{HNO}_3$  is too high.

## Example #5

Using 50 gms. of ammonium sulfate in the same general manner in place of the 50 parts of  $\text{NH}_4\text{NO}_3$  of Example #1 gave a yield of 101 gms. of cyclo-trimethylenetrinitramine or about 91% of theory. This amount of  $(\text{NH}_4)_2\text{SO}_4$  is equivalent to about 12.9 parts  $\text{NH}_3$  to 858 parts of 100%  $\text{HNO}_3$  or 1 part  $\text{NH}_3$  per 66.5 parts of 100%  $\text{HNO}_3$ .

*Example #6*

Using 75 gms. of ammonium sulfate instead of the 50 gms. in Example #5, a yield of only 70 parts or about 63% of theory was obtained, indicating that this proportion, 1 part  $\text{NH}_3$  per 44 parts 100%  $\text{HNO}_3$  is too much.

*Example #7*

Using 100 gms. of ammonium sulfate and proceeding in the same manner as in Example #6 gave a yield of only 61% of theory.

It will be noted that I may use nitric acid of any strength capable of converting hexamethylenetetramine to cyclo-trimethylenetrinitramine, that is, any strength above, about 80%  $\text{HNO}_3$ . In this specification, the term "concentrated nitric acid" is used for any nitric acid of about 80% or more  $\text{HNO}_3$  content.

Also, I may vary the proportion of hexamethylenetetramine to  $\text{HNO}_3$  over a wide range. I prefer, however, a ratio of 8 parts hexamethylenetetramine to 100 parts of  $\text{HNO}_3$ . I may use any temperature of nitration from below  $0^\circ \text{C}$ . to about  $50^\circ \text{C}$ ., although I prefer to use the range of about  $5^\circ \text{C}$ . to about  $30^\circ \text{C}$ ., and I may use a mixture of the ammonium salts mentioned above provided the total  $\text{NH}_3$  content of the added mixture does not exceed about 1 part of  $\text{NH}_3$  for about 50 parts of 100%  $\text{HNO}_3$ .

I wish to emphasize that the amount of ammonium salts used in my process should not exceed a critical upper limit. This limit varies somewhat with the temperature of nitration and strength of the nitric acid used. I consider the limit as being not more than about 1 part of  $\text{NH}_3$  equivalent of the ammonium salt used per 50 parts of 100%  $\text{HNO}_3$ . If more than this amount of ammonium salts is used the yield of cyclo-trimethylenetrinitramine obtained is lessened.

It should also be noted that a small amount of ammonium nitrate is formed in the normal nitration of hexamethylenetetramine with  $\text{HNO}_3$  and that the present invention is intended to cover a process of nitration in which an added amount of  $\text{NH}_4\text{NO}_3$  or  $(\text{NH}_4)_2\text{SO}_4$  is present in the nitrating acid, the ammonium salts being added before or during the addition of the hexamethylenetetramine to the nitrating bath.

Also, ammonium nitrate when present in the nitrating acid as the latter is being poured into water to precipitate the cyclo-trimethylenetrinitramine prevents the usual rise in temperature and in this respect produces an additional, useful result.

Also, the presence of ammonium nitrate or ammonium sulfate in the nitrating bath lessens the tendency for decomposition in the bath and permits a higher temperature to be used for the nitration. This in itself is an important contribution since the literature upon the nitration of hexamethylenetetramine has shown that the nitration often becomes uncontrollable and the bath must then be prematurely discharged into water to avoid serious accident. This tendency for decomposition is exceptionally great because of the formation of  $\text{CH}_2\text{O}$  from the methylene groups within the hexamethylenetetramine ring and the relative ease with which  $\text{CH}_2\text{O}$  is attacked by concentrated nitric acid.

The function performed by the ammonium salts mentioned is not known, but it is known

that all ammonium salts do not improve the yield of cyclo-trimethylenetrinitramine. Thus, for example, the addition of ammonium chloride does not cause any improvement in yield. It is believed that the function of the added ammonium salts is to alter the nature of the forces binding the water which is liberated during the nitration and this in turn partially prevents the hydrolysis of the hexamethylenetetramine to  $\text{CH}_2\text{O}$ . I wish to emphasize that this theory is presented merely for purposes of clarity and completeness and is not intended to limit my invention in any way not indicated by the appended claims.

I claim:

1. The process for the nitration of hexamethylenetetramine to cyclotrimethylenetrinitramine which comprises reacting hexamethylenetetramine with concentrated nitric acid containing an added amount of an ammonium salt selected from the group consisting of ammonium nitrate and ammonium sulfate at a nitrating temperature; said amount of ammonium salt being not more than the equivalent of about one part by weight of  $\text{NH}_3$  per 50 parts of 100%  $\text{HNO}_3$ ; adding the reaction mixture, with stirring, to an excess of cold water and filtering off the cyclotrimethylenetrinitramine which precipitates.

2. The process for the nitration of hexamethylenetetramine to cyclotrimethylenetrinitramine which comprises adding hexamethylenetetramine, with stirring, to a concentrated nitric acid at a temperature of less than  $50^\circ \text{C}$ ., said nitric acid containing an added amount of an ammonium salt selected from the group consisting of ammonium nitrate and ammonium sulfate, said amount of ammonium salt being not more than the equivalent of about one part (by weight) of  $\text{NH}_3$  per 50 parts of 100%  $\text{HNO}_3$ ; adding the reaction mixture, with stirring, to an excess of cold water, filtering off the cyclo-trimethylenetrinitramine, washing the latter with water and drying.

3. The process for the nitration of hexamethylenetetramine to cyclotrimethylenetrinitramine which comprises adding, with stirring, about 8 parts, by weight, of hexamethylenetetramine to about 100 parts, by weight, of about 98%  $\text{HNO}_3$ , at a temperature between about  $5^\circ \text{C}$ . and  $30^\circ \text{C}$ .; said nitric acid containing in solution an added ammonium salt selected from the group consisting of ammonium nitrate and ammonium sulfate, such addition being in an amount not greater than the equivalent of about one part (by weight) of  $\text{NH}_3$  per 50 parts of 100%  $\text{HNO}_3$ ; adding the nitration mixture, with stirring, to an excess of cold water, filtering off the cyclo-trimethylenetrinitramine, washing the latter with water and drying.

4. The process for the nitration of hexamethylenetetramine to cyclotrimethylenetrinitramine which comprises adding, with stirring, about 8 parts, by weight, of hexamethylenetetramine to about 100 parts, by weight, of about 98%  $\text{HNO}_3$ , at a temperature between about  $5^\circ \text{C}$ . and  $30^\circ \text{C}$ .; said nitric acid containing in solution about 3 parts, by weight, of added ammonium nitrate; adding the nitration mixture, with stirring, to an excess of cold water, filtering off the cyclo-trimethylenetrinitramine, washing the latter with water and drying.

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