

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Method of producing Cyclotrimethylene Trinitramine

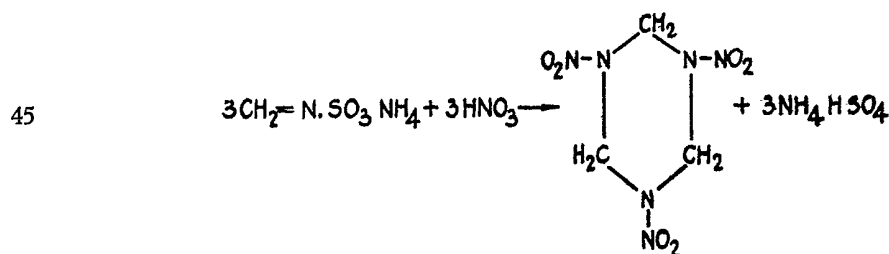
We, WASAG-CHEMIE AKTIENGESELLSCHAFT, of 9, Rolandstrasse, Essen, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a method for producing cyclotrimethylene trinitramine.

It is known that cyclomethylene trinitramine can be prepared by nitrating potassium methylene-aminosulphonate with mixed sulphuric and nitric acids. The spent acid from this process contains potassium bisulphate and cannot therefore be denitrated in the usual manner for the recovery of sulphuric and nitric acid. The sulphuric acid must be recovered by distillation and the potassium bisulphate which remains is nearly useless. Since potassium hydroxide or potassium salts which are rather expensive are again required for the

preparation of potassium aminosulphate, it has already been proposed to use the potassium sulphate recovered from the spent acid for preparing this initial substance, but the processes involved are complicated as well as difficult, or the yields are low. The following method has, for instance, been adopted. Potassium aminosulphonate obtained from ammonia and sulphur trioxide is transformed into the calcium salt, and the latter is reacted to form potassium sulphamate with the waste potassium bisulphate or sulphate. The difficulties arising in the processing of the secondary products make this method complicated and involve a considerable number of procedural steps.

It has now been found that it is also possible to obtain excellent yields of cyclotrimethylene trinitramine by nitrating ammonium methylene-aminosulphonate which is stated in the literature readily to decompose. The reaction can be represented by the following equation:



Ammonium methylene-aminosulphonate is obtained by reacting ammonium aminosulphonate with formaldehyde. According to the literature it is precipitated by means of alcohol from the aqueous solution which first arises. However, it can also be directly crystallised from its aqueous solution without the use of a precipitant, such as alcohol, if the concentrations used are high enough. These can be established by careful concentration of dilute solutions, or the concentrations used in the preparation of the ammonium methylene-aminosulphonate must be high enough to exceed the [Price 4s. 6d.]

saturation point. For instance, by introducing solid ammonium aminosulphonate into a commercial, approximately 40%, solution of formaldehyde preferably maintaining a temperature below 50°C and even better below 40°C, at a pH between 3 and 7, preferably between 4 and 5, a solution is obtained from which the ammonium methylene-aminosulphonate crystallises, partly at room temperature and in greater quantities at lower temperatures. By evaporation at room temperature or by the careful application of heat, preferably in a vacuum, at temperatures not exceeding 50°C

and preferably less than 40°C, the mother liquor can be completely evaporated and excellent yields of the salt obtained. Naturally, reaction solutions may be evaporated without previous evaporation of salt. A particularly pure salt will be obtained if its aqueous solution is vaporised by atomising it with preferably warm gases, such as air. The solid salt can also be obtained by using drum-type vacuum evaporators.

In the preparation of the ammonium methylene-aminosulphonate a pH of 5 can be very readily maintained if the process is continuously performed. Evaporation, especially atomisation, is advantageously continuously performed. Residual mother liquor can be decomposed and used, simply by boiling it with ammonium sulphate and formaldehyde.

The nitration of the ammonium methylene-aminosulphonate can be carried out with concentrated nitric acid, preferably containing  $\text{SO}_3$ , or with mixed acids, possibly in the presence of ammonium nitrate. The reaction readily proceeds between  $-30^\circ\text{C}$  and  $+30^\circ\text{C}$ , preferably between  $0^\circ\text{C}$  and  $+20^\circ\text{C}$ , and lends itself to continuous operation. Some of the cyclotrimethylene trinitramine crystallises during the process of nitration, dilution with water precipitating the remainder. The raw product is already very pure and melts at  $200^\circ\text{C}$  and above.

The spent acid from the method according to the invention can be directly processed into a mixture of ammonium sulphate and ammonium nitrate, for instance into ammonium sulphate saltpetre ( $2\text{NH}_4\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$ ) or mixed fertilizers, or it can be decomposed by conventional denitration into nitric acid and ammonium bisulphate or a sulphuric acid containing ammonium bisulphate which latter can be used for preparing ammonium sulphate. The secondary and waste products which arise in this method can all be utilised by submitting them to normal technological processes.

The invention will now be illustrated by the following Examples:—

#### EXAMPLE 1

50 parts by weight of ammonium methylene-aminosulphate are introduced, at a temperature of  $10-15^\circ\text{C}$ , into 100 parts by weight of a mixed acid containing 80% nitric acid and 20%  $\text{SO}_3$ , the mixture being well stirred during the introduction.

Stirring is continued for another 30 minutes at  $20^\circ\text{C}$  after the addition has been made, and the mixture is then poured onto ice. The yield of cyclotrimethylene trinitramine is practically quantitative. The raw product melts at  $201^\circ\text{C}$ .

The spent acid was neutralised with ammonia and evaporation of the liquor gave 155 parts by weight of a salt mixture comprising about 45% of ammonium nitrate and 55% of ammonium sulphate. This salt mixture

could be used as a fertiliser.

#### EXAMPLE 2

50 parts by weight of ammonium methylene-aminosulphonate are introduced at a temperature of  $5^\circ\text{C}$  to  $10^\circ\text{C}$  into 100 parts by weight of a well stirred anhydrous nitric acid. Stirring is continued for 30 minutes at room temperature after this addition has been made, and the mixture is then poured on to ice. The yield of cyclotrimethylene trinitramine is about 75%, the raw product melting at  $201^\circ\text{C}$ .

The spent acid was evaporated to dryness, whereupon 46 parts by weight of ammonium bisulphate were obtained. The distillate consisted of 222 parts by weight of an approximately 30% nitric acid which could be reused in the process after concentration thereof. The ammonium bisulphate can be used for the production of ammonium sulphate by supplying it to an ammonia saturator.

#### WHAT WE CLAIM IS:—

1). A method of preparing cyclotrimethylene trinitramine, which comprises nitrating ammonium methylene-aminosulphonate.

2). A method as claimed in Claim 1, wherein spent acid from the reaction which contains ammonium bisulphate is processed in known manner into technologically useful ammonium salts, such as ammonium sulphate saltpetre or mixed fertilisers.

3). A method as claimed in Claim 1, wherein spent acid from the reaction is evaporated to remove the nitric acid therefrom, and wherein the residue is processed in known manner into ammonium sulphate or mixed fertilisers.

4). A method as claimed in any preceding claim, wherein the nitration reaction is carried out at a temperature in the range of  $-30^\circ\text{C}$  to  $+30^\circ\text{C}$ .

5). A method as claimed in any preceding Claim, wherein the nitration reaction is carried out at a temperature in the range of  $0^\circ\text{C}$  to  $+20^\circ\text{C}$ .

6). A method as claimed in any preceding Claim, wherein the reaction mixture is diluted with water to precipitate the cyclotrimethylene trinitramine.

7). A method as claimed in any preceding Claim, wherein the nitration reaction is performed continuously.

8). A method of preparing cyclotrimethylene trinitramine substantially as hereinbefore described in either of the foregoing Examples.

9). Cyclotrimethylene trinitramine whenever prepared by the method claimed in any preceding Claim.

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