

# A SINGLE STAGE PROCESS FOR THE PREPARATION OF CYCLOTETRAMETHYLENE TETRANITRAMINE

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A single stage process for the preparation of Cyclotetramethylene tetranitramine ( $\beta$ -HMX) has been developed. The ingredients (i) Hexamine in glacial acetic acid, (ii) Ammonium nitrate in nitric acid and (iii) acetic anhydride were simultaneously added to glacial acetic acid medium maintained at 45°—48° with stirring. The crude yield of the product per 100 gm. of hexamine used is 120 gm having the melting point 265—266°C. Purified from acetone the substance melts at 272°—275° and passes standard vacuum stability and impact sensitivity tests.

Cyclotetramethylene tetranitramine, known as HMX is the most powerful modern high explosive. It has higher density and detonation velocity than the corresponding explosive cyclotri-methylene trinitramine called RDX.  $\beta$ -HMX, therefore, finds special applications.

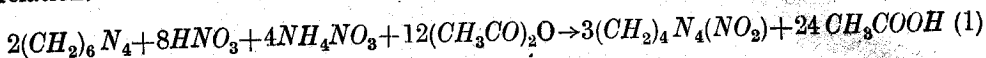
HMX has been prepared by Bachmann *et al*<sup>1</sup> by a two-stage process. In the first stage Dinitro-pentamethylene tetramine (DPT) is prepared as an intermediate by the action of a mixture of nitric acid and acetic anhydride upon hexamine dissolved in glacial acetic acid. In the second stage the DPT is further nitrated by adding to its suspension in acetic anhydride, a solution of ammonium nitrate in 98 per cent nitric acid. On crystallisation from acetone the pure HMX, with the melting point at 281—282°C was obtained.

Recently Picard<sup>2</sup> patented a method for the preparation of HMX by adding (i) a solution of hexamine in acetic acid and (ii) a mixture of nitric acid and ammonium nitrate to acetic acid-acetic anhydride medium containing paraformaldehyde as catalyst and maintained at 44+1°C. The reactions require ageing of different periods at two stages. A yield of 200 gm crude product from 101 gm hexamine is claimed.

The two stage Bachmann process is time consuming and offers poor yield. Picard<sup>2</sup> processes requires intervals and definite ageing periods. Both the processes use large quantities of acetic anhydride (more than 500 cc per 100 gm. of hexamine used). Since the reagents in both the stages of Bachmann's process are the same except the addition of ammonium nitrate in the second stage, it was thought possible to combine the two stages to develop a single stage process by adjusting the quantities of the ingredients used, with the conditions of the experiments suitably modified assuming that the reactions involved follow

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the relation.



Finally a single stage process was developed for the preparation of the explosive **HMX** using the reagents in approximately stoichiometric quantities.

#### MATERIAL AND METHOD

*Method*—Two solutions were made in the following ways :

(i) 60 gms of Hexamine (BDH) was dissolved in 100 cc of glacial acetic acid (AR) and

(ii) 72 gms of ammonium nitrate (Pure) dried at 105°C were dissolved in 110 cc of Nitric acid (94% C.P.) cooled to a temperature below 20°C during additions.

The solutions (i) and (ii) and the required quantity of acetic anhydride (280 cc) were taken in three separate burettes and delivered simultaneously in a continuous stream at controlled rates to a stainless steel reaction vessel containing 600 cc of glacial acetic acid together with 10 gm of ammonium nitrate and 20 cc of acetic anhydride and maintained at the temperature of 45° to 48°C throughout the operation with constant stirring. A water bath used for the purpose was initially maintained at 25° to 30°C as large amount of heat was evolved during the reaction. Subsequently slight warming was required to maintain reaction temperature.

After completion of additions the reaction mixture was stirred at the same temperature for one hour when 250 cc of hot water (at 85°—90°C) were added and the stirring was continued for further five minutes. The reaction mixture was then transferred to a two-litre flask and refluxed for one hour, after which it was allowed to cool slowly to room temperature with occasional stirring. The product was collected on filter paper and washed free from acid with hot water. Crude yield obtained was 72 gm. *i.e.* 120 gm. per 100 gm. of Hexamine.

The material was re-crystallized from acetone twice and the re-crystallized material was examined with respect to melting point, vacuum stability and density.

*Impact Sensitivity*—The sensitivity to impact of the  $\beta$ -HMX samples was carried out in a Picalinny Arsenal type apparatus using 1 kg. weight. The statistical methods of Naval Ordnance Test Station<sup>3</sup> (U.S.A.), were used to interpret the test results and to obtain the 50% explosion weight.

*Vacuum Stability*—This was measured in a standard Vacuum Stability apparatus. The data indicate the amount of gas evolved, expressed at N.T.P. when one gm. of the explosive is exposed under vacuum to a temperature of 150°C for 48 hours\*.

*Density*—Density was determined by using a specific gravity bottle employing methyl alcohol (A.R.) as the medium.

\* According to the standard specification 5 gm. of the explosive under these conditions should not evolve more than 2 cc of gas.

## RESULTS AND DISCUSSION

The melting point of the crude product was found to be  $265^{\circ}$ — $266^{\circ}$ C. At least two crystallizations are required to obtain a product melting at  $272^{\circ}$ — $275^{\circ}$ C that will stand the vacuum stability test and possess an impact sensitivity of 56 cm. The results of a few experiments are given in Table I.

The single stage method described here gives higher yield of HMX (120 gm/100 gm hexamine) compared with the two-stage Bachmann process<sup>1</sup> (75 gm/100 hexamine) but less than that reported by Picard<sup>2</sup>. However the new process described economises on the use of acetic anhydride as well as on the time of operation and also dispenses with the use of catalyst and the ageing period<sup>2</sup>. The quantities of the re-agents used in the present method are based on the stoichiometric relation I. During the development stages, however, slight deviations in the quality of the reagents used have been made to obtain better quality of the product. More acetic anhydride than that required by the relation I has been used to make up for the lower strength of the nitric acid (94%) used in the present investigation.

TABLE I

MELTING POINT AND CRUDE YIELD OF HMX WITH IMPACT SENSITIVITY, VACUUM STABILITY AND DENSITY. IN ALL THE EXPERIMENTS HEXAMINE USED IS 60 GMS AND NITRIC ACID (94%) 150 GMS.

Serial No.	Amm. Nitrate (gm)	Acetic anhydride (c.c.)	Acetic Acid (c.c.)	Melting point crystallised ( $^{\circ}$ C)	Yield of crude HMX per 100 gm of Hexamine (gm)	Impact Sensitivity in cm (1 Kg. wt.)	Vacuum stability for 48 hours at $150^{\circ}$ C (c.c. per gm)	Density
1	80	290	580	272	120	..	..	..
2	78	290	580	272	121.7	46.0	0.048 0.11	1.901
3	78	300	580	272	120	..	0.38 0.38	..
4	80	290	700	272- 273	121.0	63.0 57.0	0.28 0.34	1.890
5	82	310	750	272- 273	125.0	61.0 65.0	0.30 0.36	1.90
6	82	300	700	275	119.1	..	..	..

## ACKNOWLEDGEMENT

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## REFERENCES

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