

It is prepared through the addition of a solution of Hexamine (10g, 0.07mol) in distilled water (17.5ml, 0.972mol) drop by drop to nitric acid (specific gravity =1.4, 11.75ml, 0.261mol) already present in the above-mentioned setup. The reaction temperature was fixed at 15°C and the rate of addition of Hexamine solution was controlled to meet this condition. Finally the mixture was cooled to 5°C and Hexamine Dinitrate was separated from the reaction mixture using a vacuum pump and dried in a vacuum oven. To a mixture formed of glacial acetic acid (5ml, 0.0874mol) and acetic anhydride (2ml, 0.0212mol), hexamine dinitrate (1g, 0.00375mol) was added as one portion. Then the reaction mixture was left, for a fifteen minute period, at a temperature of (44°C) which was also maintained throughout this procedure. The reaction mixture was then quenched by chilling it to 12°C. Rapid separation of the solid phase was then carried out.

The reactor vessel was a 1000 ml. flask fitted with a cover containing four ground glass connections. and a mechanical stirrer. The reactor vessel was surrounded by a temperature-controlled water bath and contained a stainless steel cooling coil for cooling the reaction mixture. The acetic acid, acetic anhydride and the HNO<sub>3</sub>-NH<sub>4</sub>NO<sub>3</sub> solution were introduced through three of the ground glass connections, while cooling or heating water, as required, was circulated through the cooling coil via the fourth glass connection.

50.6 grams of glacial acetic acid, 4.1 grams of acetic anhydride and 4.0 grams of hexamine were charged to the reactor vessel to serve as a heel. An analysis of the heel showed that it contained excess acetic anhydride at this point. The temperature of the reactor contents was then raised to 43°C and maintained thereat during the remainder of the run.

The first addition of the reagents was made by introducing into the reactor vessel continuously and proportionately during 21 minutes 53.4 grams of a 38% hexamine solution consisting of 20.3 grams of hexamine and 33.1 grams of glacial acetic acid, 33.2 grams of a 56.4% HNO<sub>3</sub>-NH<sub>4</sub>NO<sub>3</sub> solution consisting of 18.7 grams of HNO<sub>3</sub>, and 14.5 grams of NH<sub>4</sub>NO<sub>3</sub>, and 105.7 grams of acetic anhydride. The reaction mixture was then aged for 6 minutes before the second addition of reagents was made.

The second addition was performed in two parts: Part 1 consisted of adding 10.5 grams of a 56.4% HNO<sub>3</sub>-NH<sub>4</sub>NO<sub>3</sub> solution consisting of 5.9 grams of HNO<sub>3</sub>; and 4.6 grams of NH<sub>4</sub>NO<sub>3</sub>, and 34.1 grams of acetic anhydride to the reactor vessel continuously and proportionately during 7 minutes; Part 2 following Part 1 consisted of adding 41.3 grams of the 56.4% HNO<sub>3</sub>-NH<sub>4</sub>NO<sub>3</sub> solution consisting of 23.3 grams of HNO<sub>3</sub>; and 18.0 grams of NH<sub>4</sub>NO<sub>3</sub>, and 129.1 grams of acetic anhydride to the reactor vessel continuously and proportionately over a period of 8 minutes.

When the second addition was complete, the reaction mixture was aged for 30 minutes. Thereafter the reaction mixture was transferred to another vessel and mixed with sufficient dilute aqueous acetic acid to hydrolyze any excess acetic anhydride and reduce the concentration of the mixture to 80 weight percent acetic acid. The diluted reaction mixture was heated at 110°C for one hour to effect the usual simmering operation to eliminate by-products, notably linear nitramines formed during the reaction, then cooled to 30°C and filtered to separate the HMX product, which was washed with cold water and dried.

In accordance with this example and in order to start up the process, the first nitrator was charged with a starting heel of 300 ml. of glacial acetic acid, 25 ml. of acetic anhydride and 8g of paraformaldehyde. These charged materials in the first nitrator were brought up to a temperature of about 44°C. There was then continuously fed into the first nitrator hexamine dissolved in acetic acid (90.4% acetic acid) at the rate of about 101 grams per minute. Ammonium nitrate is dissolved in nitric acid, which may be approximately 50 degrees Baumé, to form a solution containing 56.4% nitric acid.

This solution was fed into the first reactor through a separate conduit at the rate of 22.0 grams per minute. Acetic anhydride (97.5% minimum purity) was fed into the nitrator through another conduit at the rate of 53.3 grams per minute. While maintaining reaction at approximately the aforementioned 44°C temperature, the ingredients were subjected to vigorous agitation. As earlier mentioned, the incoming feed materials are preferably passed through a constant temperature bath to preheat them and maintain them at a uniform temperature of 40°C as they are being fed into the first nitrator as this permits more accurate feed control. After about 15 minutes reaction time at the temperature of about 44°C in the first reactor, a certain portion of the ingredients had reacted. Therefore, reaction product was then continuously withdrawn from the first reactor to the first age pot.

In the first age pot the withdrawn reaction materials were agitated and maintained at a temperature of about 44°C for about 15 minutes. In this first age pot continued reactions and/or further reactions took place to essentially complete the formation of intermediate products thereby improving the overall yield of HMX from the process.

From the first age pot the reaction products were then further ingredients were introduced as follows: ammo withdrawn to the second nitrator. In the second nitrator further ingredients were introduced as follows: ammonium nitrate dissolved in nitric acid (56.4% nitric acid) at the rate of 33.1 grams per minute; acetic anhydride (97.9% anhydride) at the rate of 76.8 grams per minute. These incoming ingredients were passed through a constant temperature bath in order that the temperature was raised and held at about 40°C. The reaction mixture in the second nitrator was agitated vigorously and maintained at a temperature of about 44°C.

The addition of these further ingredients in the second nitrator effected the second stage of nitration which is essential to the formation of HMX. Further nitration to HMX of intermediates formed in the first nitration stage occurs in the second nitrator. After about 4 minutes reaction time in the Second reactor, products containing HMX were withdrawn from the reactor to a surge tank. The products are agitated and maintained at 44°C in the surge tank. At 30-minute intervals, the contents of the surge tank were pumped to one of the final age pots. In these age pots the final reaction mixture is aged for 60 minutes with vigorous agitation while the temperature is controlled at 44°C, thereby permitting the formation of HMX to approach completion.

The hydrolysis of the excess acetic anhydride and the unstable reaction by-products is effected by the addition of 1500 ml, of water to the final age pot and by heating the aqueous mixture to 98-102°C in which range the temperature is maintained for 30 minutes. The product slurry is cooled to 30°C and filtered with large Bichner funnels being used to recover the crystalline product which was washed with water until free of acid. The cake was then dried by heating in a steam oven. In operation in accordance with this Example I for two hours and ten minutes, the effluent from the second nitrator was collected for one hour and thirty minutes from which 991.6 grams of crude HMX were obtained. The average purity of this HMX was 73%, the remainder being RDX. The yield was 0.84 gram of pure HMX produced per gram of hexamine consumed. All HMX crystals were beta-HMX.

785 grams glacial acetic acid, 13 grams acetic anhydride and 17 grams of paraformaldehyde were added to a suitable flask (6 to 10 liters) equipped with stirrer, thermometer and three dropping funnels. The temperature of the reaction was maintained at 44°C. By means of a water bath. 320 grams acetic anhydride, 180 grams nitric acid-ammonium nitrate solution and a solution of 101 grams hexamine dissolved in 165 grams acetic acid were then added to the reaction mixture via dropping funnels over a period of 15 minutes with constant stirring of the reaction mixture. The nitric acid-ammonium nitrate solution was prepared by dissolving 233 grams ammonium nitrate in 218 grams of nitric acid (99% or better). This latter solution should be kept above 20°C to prevent crystallization of ammonium nitrate from solution.

The hexamine and nitric acid solutions were added continuously and proportionately. After the addition of 66.5 grams of the hexamine solution, 64 grams of the acetic anhydride were added in bulk. A similar amount of the anhydride was added after the addition of each 66.5 grams of the hexamine solution except that after all the hexamine had been added a final addition of 128 grams of acetic anhydride was made to bring the total up to 320 grams. After the addition of the above ingredients, the reaction mixture was aged for approximately 15 minutes. After the aging period, 480 grams acetic anhydride and 271 grams nitric acid-ammonium nitrate solution were added over a fifteen minute period in the following manner; 320 grams acetic anhydride and 271 grams nitric acid-ammonium nitrate solution were added continuously and proportionally and then 160 grams acetic anhydride in bulk. The reaction mixture was again allowed to age, this time for a period of about one hour.

After aging, purification of the product may be accomplished by the addition of hot water and refluxing the mixture for about an hour. In this instance the mixture was poured into a 7-10 liter flask equipped with a suitable reflux condenser. 350 grams of hot water (75-90°C) were added to the flask and the reaction mixture heated at reflux for 30 minutes. The reaction mixture was then cooled to about 20°C. by means of an ice bath and the addition of approximately 2000 grams of ice to the mixture. The resulting water insoluble material was filtered out and washed with three portions of cold water amounting to about 400 grams each. The product was then dried. The crude yield was approximately 200 grams or 95% of theoretical. The purity of the product was better than 90% HMX, the residue being largely RDX.

The product obtained through the above process is a white solid having crystal-like needles and is the alpha form of HMX. The alpha form may be easily converted to the beta form by crystallization from a hot solvent solution such as acetone, acetonitrile or cyclohexanone using equal parts by weight of the alpha HMX and the solvent. The resulting white crystals of beta HMX melt at 278-279°C and have a purity of 99% or better.

The proportions of the various reactants recited in the above specific example are not to be considered as limiting the scope of the process of this invention. The mole ratios of nitric acid and ammonium nitrate used to prepare the HMX may be varied from 5 to 7 moles and from 3 to 5 moles respectively per mole of hexamine. The acetic anhydride may be varied in mole ratio between 10 and 11 moles per mole of hexamine. The paraformaldehyde may be added to the acetic acid acetic anhydride solution in quantities of from 0.27 to 0.54 mole per mole of hexamine. The preferred reaction temperature ranges between 40 and 48°C.

Urea, 6 g (0.1 mol), was added in portions to a mixture of 22.5 g of 98% nitric acid and 22.5g of oleum (20 % SO<sub>3</sub>) at -5 to 0°C under continuous stirring. After the addition the mixture was stirred for 1h at 0 to 5°C and poured into 30 g of an ice-water mixture, and 50 mL of a 37 % formaldehyde solution was added at a temperature not exceeding 20°C. The mixture was heated to 35°C, stirred for 30 min, cooled, and neutralized to pH 6 with 25 % aqueous ammonia at 20-25°C. It was then stirred for 45 min at 20°C, and the precipitate was filtered off, washed with water, and dried at room temperature until constant weight. Yield 14.7 g (67.4 %, calculated on urea), m.p. 209-210°C; published data: 205-206°C. The nitration of urea was carried out as described above. After keeping stirring for 1h at 0 to 5°C, the mixture was poured into 30g of an ice-water mixture, maintaining the temperature below 10°C. The mixture was extracted with ethyl acetate (4×30 mL), and the extract was washed with water (3×20 mL), kept for 2h at 20°C, and evaporated to dryness under reduced pressure. The product was dissolved in 20 mL of ether, and the solution was poured into 250 mL of hexane, and the precipitate was filtered off. Additional recrystallization from dichloroethane and 2-propanol (9:1) gave nitramide. Yield 7.56 g (61.0 %, calculated on urea), m.p. 80-81°C. The nitration of urea was carried out as described above. After keeping stirring for 1h at 0 to 5°C, the mixture was poured into 30 g of an ice-water mixture, and 50ml of a 37% formaldehyde solution was added at a temperature not exceeding 20°C. The mixture was heated to 35°C, stirred for 30min, cooled, and extracted with ether (5×50ml). The extract was dried over MgSO<sub>4</sub>, and the solvent was distilled off under reduced pressure to obtain a yellowish oily substance. Yield 11.3g (46.3%, calculated on urea).

To 100 ml of HNO<sub>3</sub> (density 353g/ml or 53% conc.), cooled to +10°C, was sprinkled 50g of sulfamic acid, a temperature rise is not observed. After mixing with stirring at 10°C for 30 minutes, 53g of DNU was made, the temperature is kept below 20°. After holding at this temperature for 20 minutes, the reaction mixture was warmed to 30°, then external heating was discontinued, but the reaction continued to increase in temperature by itself. After reaching 35-36° it was carried on to be gently cooled to 30°C under running tap water. The temperature again continued to increase after reaching 35-37°, and the mixture was again cooled to 30-33°, and so on for as long as the temperature kept increasing. The reaction mixture was cooled to 15°, and it becomes more viscous during this time. After dilution with 300ml of cold water, neutralization of sodium bicarbonate was carried out to pH = 6, by the end of the neutralization of the solution became dull, and formed a number of ne-grained sediment. After an exposure of 1 hour the solution was filtered, the precipitate was washed first with water and finally with isopropyl alcohol to facilitate drying. The mass of dry product was 3.5g or about 8% of the theoretical value (assuming the formation of DPT 1 mol to 1 mol DNU). The nature of combustion of the sample did not differ from the standard DPT. The measured melting point temperature of the sample amounted to about 195-198°C. DPT obtained by the other more traditional method has a melting point of 200-201°C.

The concentration of nitric acid 70% (density 1.411g/ml). All procedures are identical to experiment number 8, but with the following differences: the amount of sulfuric acid is reduced to 20 ml, after the termination of heat the reaction mixture of the porridge thickens much faster and at lower temperature, no more than about 25-30°C. The yield of DPT in this experiment was 21 g or 96.3% of the theoretical (assuming the formation of 1mol DPT to 1mol DNU). When doing this experiment two additional times, the yield was 20g and 20.5g, respectively, which was consistently above 90% yield. The products obtained by this method were in the temperature range of 198°C.

The concentration of nitric acid was about 63% (density 1.386g/ml). A mixture of 50 ml of nitric acid and 35 ml of sulfuric acid (92.5% concentration, density 1.825g/ml), which was cooled to 0°C, was introduced with stirring 25g of sulfamic acid. The temperature rose to 5°C. After maintaining the temperature for 20 minutes at 0°C, 27g of DNU started to be added in small portions with stirring, keeping the temperature below 15°C. The reaction mixture was then kept at 5-10°C for 40 minutes, while continuing stirring. The mixture was then gently heated to 30 °C, then heating was stopped, but the temperature continued to increase by itself, as in the previous experiments. Just as before, the temperature was allowed several times to reach 38-42°C, and at such times the temperature was brought back down to 35°C by cooling. When heat ceased to occur (in about an hour after heating to 30°C), the reaction mixture was cooled to 15°C, while it thickened and became similar to the reaction mixture during cooking. More PETN was diluted 1 to 2 cold porridge, prepared in advance by the freezing of 10% aqueous solution of ammonium nitrate. This was followed by neutralization with sodium bicarbonate to a pH of ~ 6, resulting in much sediment. This was filtered, then washed with water and isopropanol. After drying, the mass of sludge was 14.2g, or 65.1% of theory (DPT 1mol to 1mol DNU). The melting temperature of the product was 194-198°C.

To a stirred solution of 20 gm. (0.091 mole) DPT, I, in 438 cc. (4.66 moles) of acetic anhydride, was added 140 cc. (3.34 moles) of 99.6% nitric acid over 40 min. at 44°C. The mixture was then cooled to 15°C and poured on ice. The filtered precipitate was washed with ethanol and air-dried to yield 31.7g, m.p. 176° to 185°C, or 87% of theoretical. Three crystallizations from nitromethane or, better, from acetone raised this to 186.5°-187.2°C

A mixture of 10 gm. (0.046 mole) of DPT (m.p. 203° to 204°C.) and 46.2 cc. (0.394 mole) of acetic anhydride was stirred at 65° to 70°C. (bath 60°C.) While a solution of 11.1g (0.138 mole) of ammonium nitrate in 13.4 cc. (0.319 mole) of 99.67% nitric acid was added over a 15 min. period. The suspension dissolved and then reappeared. After subsequent stirring for 22 min. and 10 min. at 25°C, the whole was poured into 400g of ice and water. The filtered solid, washed with 300 cc. water and air-dried, weighed 14.8g, m.p. 226° to 250°C. It was boiled with 207 cc of 70% nitric acid until strong nitrogen oxide evolution commenced. After cooling and drowning with 2 liters water, it was filtered and dried at 70°C. to weigh 8.9g (65.5% of theoretical) with melting point 267° to 268°C.

A stirred solution of 1.1g (0.014 mole) of ammonium nitrate in 1.3 cc. (0.031 mole) of 99.6% nitric acid was heated to 70-75°C in a water bath while 0.200g ( $9 \times 10^{-4}$  mole) of DPT was added. After 15 min. the mixture was drowned in ice and water, filtered, and the precipitate washed and dried. It weighed 0.15g and melted at 187.5° to 189.5°C. According to thermal analysis by the melting point composition diagram to be reported in the next paper of this series, this contained about 30% HMX, which would constitute a 17% yield; the remainder, if Cyclonite, would be 52% of the theoretical both on the 1 : 1 basis. Fractional crystallization from nitromethane yielded these two, and no other, compounds.

This ratio of HMX to RDX was shifted by decrease in amount of nitric acid (34 moles to 20 moles) and increase of ammonium nitrate to quantity equimolar with the acid. A solution of 126g of 99.6% nitric (2 moles) and 160g (2 moles) of ammonium nitrate was stirred at 68°C while 21.8g (0.1mole) of DPT was added over 20 min. After 30min. more at this temperature, the mixture was drowned in ice and water and filtered. The product melted at 197° to 202°C and weighed 13g and, according to thermal analysis, contained about 3% HMX. The yields are therefore 1.77% HMX and 57% Cyclonite. Neutralization of the liquors produced only a trace (less than 0.15%) of impure DPT.