REPORT CSD 2555-FR

INERT CARRIER PROCESS APPLICATION TO HMX NITROLYSIS AND RECRYSTALLIZATION

Volume I: HMX Chemistry

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The application of the ICP to the nitrolysis of HMX was studied. The feasibility on bench scale and pilot plant scale was demonstrated. Design parameters for a complete continuous ICP pilot plant were obtained for the production of crude HMX via DAPT/DADN/HMX technology. Each chemical step was made in the present CSD pilot plant under continuous process conditions.

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AB

SUMMARY

Picatinny Arsenal, in conjunction with Los Alamos Scientific Laboratory and the University of Idaho has been developing the new DAPT/DADN/HMX technology which involves the following reactions:

A. Hexamine is reacted with acetic anhydride in the presence of ammonium-acetate and water forming DAPT (diacetyl-penta-methylene tetramine), formaldehyde, and acetic acid.

B. DAPT is reacted with sulfuric acid/nitric acid nitration medium forming DADN(1,5,diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane), formaldehyde, and water.

C. DADN is reacted with polyhosphoric acid/nitric acid producing acetic acid and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane).

These three steps were explored on bench scale using ICP techniques. Reaction variables such as temperature, molar feed ratios, reaction time, inert carrier compatibility, and corrosion studies on materials of construction were investigated. Data developed in the bench scale study were applied directly to the pilot plant program. In the pilot plant the feasibility of using ICP was successfully demonstrated for each chemistry step.

This is the first time the new HMX chemistry has been run through any pilot plant. The third chemistry step, using the powerful new nitration media of PPA-HNO_3, presented challenging problems. The major problems that were solved are in the engineering of the reactors, feed systems, and materials of construction.

The major accomplishments of this pilot plant feasibility study are:

A. DAPT

200 lb of DAPT were prepared in the pilot plant. The final run was for 78 min at a rate of 45 lb/hr with a 109-percent yield.

B. DADN

35 lb of DADN were produced in the pilot plant. The final run was for 2 hr and 40 min at a rate of 8.5 lb/hr with a 86.5-percent yield based on hexamine. 93-percent H_2SO_4 was used instead of 98-percent H_2SO_4, which means an oleum plant is not required.

C. HMX

10 lb of HMX were prepared. The final run was for 2 hr at a rate of 3 1/2 lb/hr with a yield of 67 1/2 percent based on DADN.

It is concluded that this new chemistry is ideally suited to the ICP technique. Further pilot plant optimization is necessary with a special emphasis on the third chemical step, the nitration with HNO_3/PPA. In particular, the regeneration of PPA from spent acid should be studied.

PREFACE

This program was performed by Chemical Systems Division of United Technologies, Sunnyvale, California, 94088 under prime contract No. DAAA21-75-C-0251 for the U. S. Army Materiel Command AMCPM-PBM-EE, Dover, New Jersey 07801. The contract project officer was Thomas Caggiano.

This program was based on a company-funded effort directed by R. D. Sheeline at Chemical Systems Division.

Acknowledgement is extended to Thomas Caggiano in supplying reference materials and technical suggestions at coordination meetings and to Vic Siele of the Feltman Research Laboratories at Picatinny Arsenal for his support and competent technical assistance.

Contents

Figures

TABLES

HMX CHEMISTRY

HMX is commercially prepared at Holston Army Ammunition Plant. Although no separate production line is available, the existing RDX equipment is shifted over to HMX when it is needed.

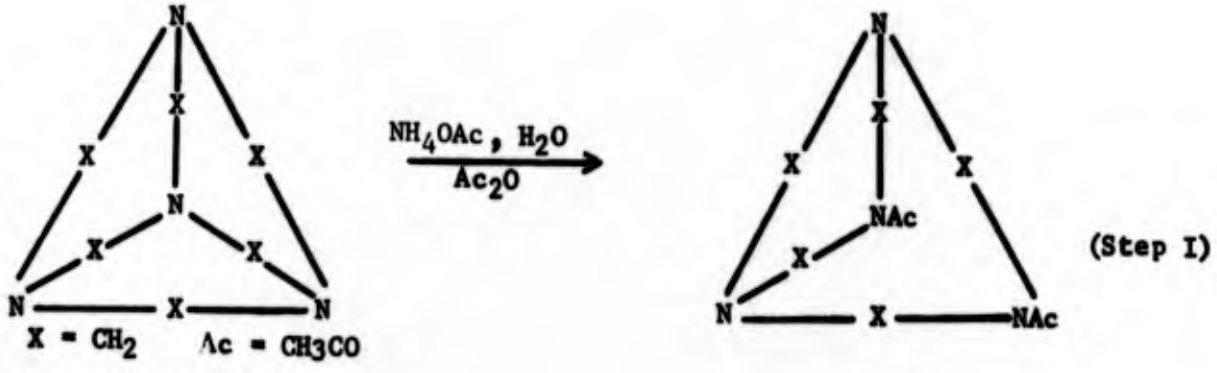
The chemistry of this reaction is:

$$\text{Hexamine} + \text{acetic anhydride} + (NH_4)NO_3 \longrightarrow \text{RDX} + \text{HMX} + \text{acetic acid}$$

HMX is produced this way with a 63 percent yield in the presence of large amounts of RDX. HMX is purified by destruction of the unwanted RDX followed by recrystallization.

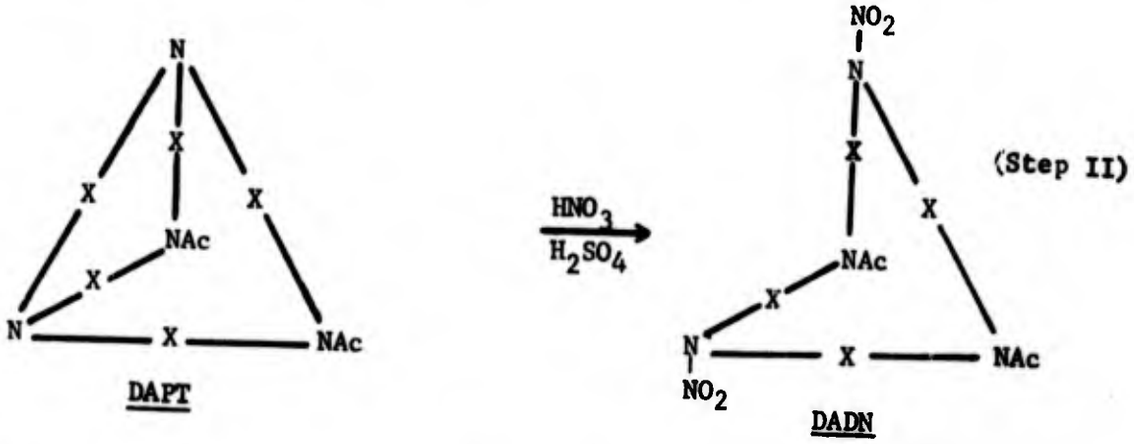
The new approach, developed by Picatinny Arsenal, is shown in the following chemical steps:

A. Hexamine (hexamethylenetetramine) is reacted with acetic anhydride in the presence of ammonium acetate and water forming DAPT (DiAcetylPentamethyleneTetramine), formaldehyde, and acetic acid. The formaldehyde is reacted in situ with ammonium acetate forming hexamine, water, and acetic acid. Ammonium acetate may be formed by the reaction of ammonia and acetic acid.

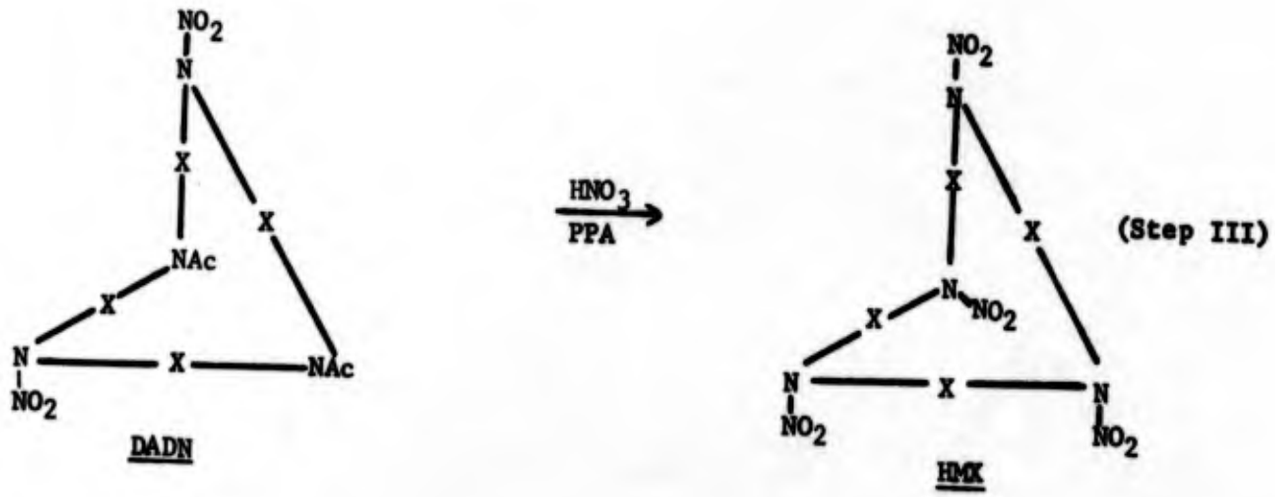


Hexamine **DAPT**

B. DAPT is reacted with a sulfuric acid/nitric acid nitration medium forming DADN(1,5-DiAcetyl-3,7-DiNitro-1,3,5,7-tetraazacyclooctane), formaldehyde, and water.



C. DADN is nitrated with a nitrolysis medium of polyphosphoric acid/nitric acid producing HMX (1,3,5,7, tetranitro-1,3,5,7, tetraazacylooctane) and acetic acid.



Unlike the process used at Holston, no RDX can be produced with this chemistry. Consequently, HMX of very high purity is produced. Better than 99-percent pure HMX has been obtained in the laboratory.

The feasibility of this chemistry was shown on a small laboratory-scale at Picatinny. The chemistry involved reactions of viscous materials and the development of exotherms. The ICP carrier effectively lowers the viscosity and also acts as a heat sink and heat exchange medium to provide excellent temperature control of the process.

Capital equipment, material cost, and labor cost needed in the economic analysis were estimated from CSD's pilot plant work.

HEXAMINE TO DAPT

The first step in the process of making HMX is shown in Equation 1. Numbers in parentheses below each compound are molecular weights, and Ac represents CH_3CO.

$$\underset{(140)}{\text{Hexamine } C_6N_4H_{12}} + \underset{(102)}{\text{Acetic anhydride } 2Ac_2O} + \underset{(18)}{\text{Water } H_2O} \longrightarrow \underset{(212)}{\text{DAPT } C_9N_4H_{16}O_2} + \underset{(30)}{\text{Formaldehyde } CH_2O} + \underset{(60)}{\text{Acetic acid } 2AcOH} \quad (1)$$

Ammonium acetate is added to the raw materials to react with the formaldehyde formed in Equation 1, above, to form additional hexamine according to Equation 2.

$$\underset{(30)}{\text{Formaldehyde } 6CH_2O} + \underset{(77)}{\text{Ammonium acetate } 4NH_4OAc} \longrightarrow \underset{(140)}{\text{Hexamine } C_6N_4H_{12}} + \underset{(18)}{\text{Water } 6H_2O} + \underset{(60)}{\text{Acetic acid } 4AcOH} \quad (2)$$

The overall reactions of Equations 1 and 2 are combined in Equation 3, which shows that a 120-percent yield (1.2 mole of DAPT from 1 mole of hexamine) can be obtained.

$$\text{Hexamine} + 2.4\ Ac_2O + .8\ NH_4OAc \longrightarrow 1.2\ \text{DAPT} + 3.2\ AcOH \quad (3)$$

An economic advantage may be obtained by preparing the ammonium acetate in situ. Ammonia will react with the acetic acid formed by Equation 3 to give ammonium acetate in accordance with Equation 4.

$$\underset{(17)}{\text{Ammonia } NH_3} + \underset{(60)}{\text{Acetic acid } AcOH} \longrightarrow \underset{(77)}{\text{Ammonium acetate } NH_4OAc} \quad (4)$$

The overall reaction using ammonia becomes:

$$\text{Hexamine} + 2.4\ Ac_2O + .8\ NH_3 \longrightarrow 1.2\ \text{DAPT} + 2.4\ AcOH \quad (5)$$

Bench Scale

These reactions have been studied very thoroughly by Picatinny Arsenal and Los Alamos Scientific Laboratories. Mole ratios were established and the yield determined by NMR techniques. Yields are of the order of 110 to 115 percent (moles DAPT/moles hexamine).

The established mole of reactants is:

Hexamine	1.0 mole
Acetic anhydride	2.6 mole
Ammonium acetate	.8 mole
Water	3.9 mole

Reaction temperature is 20° to 25°C and the reaction time is less than 10 minutes.

Under an IR&D program, this reaction was shown to be feasible in the ICP pilot plant where acetic anhydride-saturated heptane was found to be an excellent carrier.

With the above information, there was no need for additional bench scale work and the DAPT part of the program started in the pilot plant.

Pilot Plant

Two different pilot plant configurations were used. Figure 1 shows the first setup where one disperser is used. Figure 2 shows how a second disperser was used to provide better reaction time control.

Dual Dispersers - The dual disperser increases yield by preventing virtually all unreacted or partially reacted material from leaving the process. The small percentage of just added ingredients, which leaves the first disperser, is attenuated almost completely by the second.

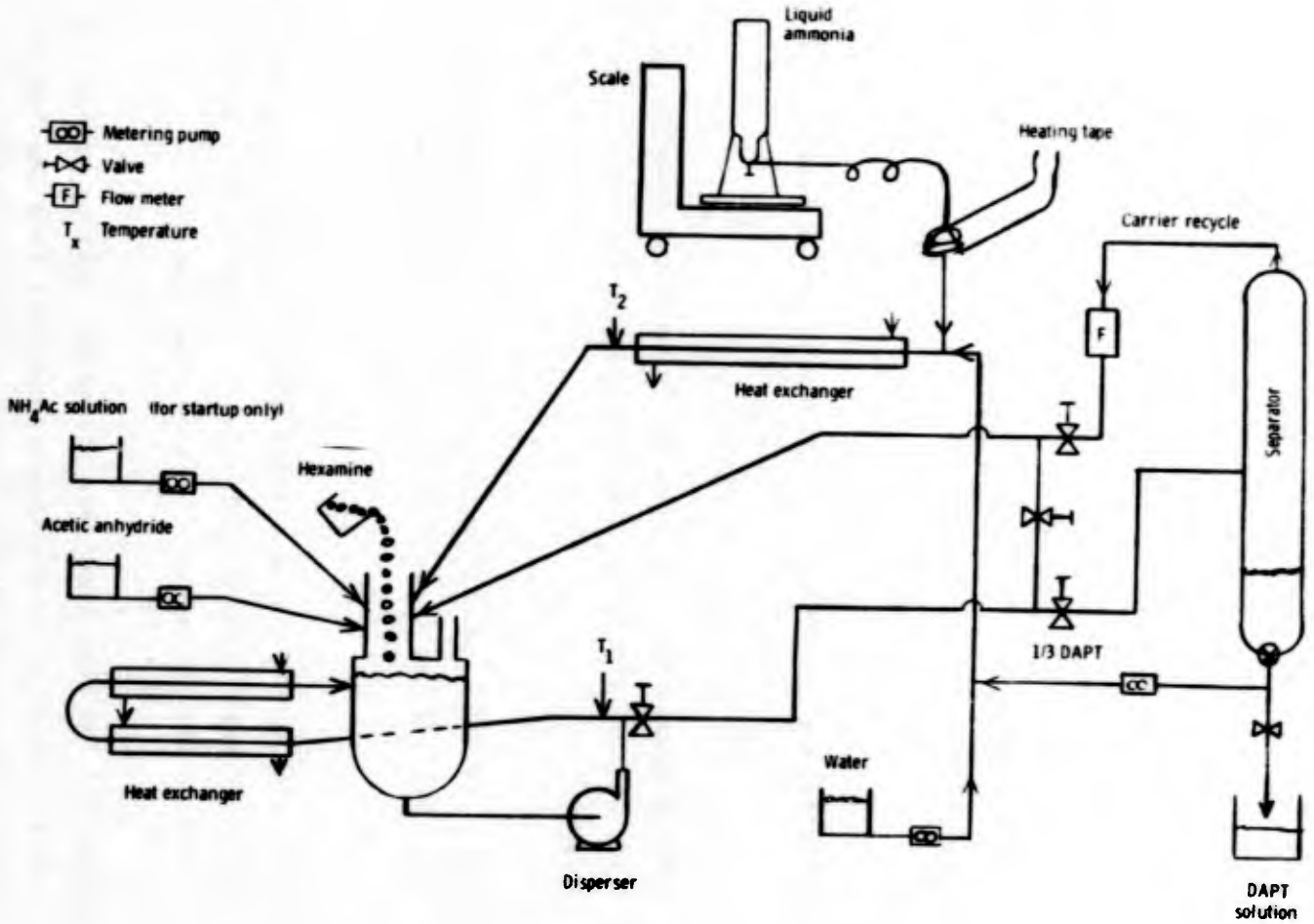


Figure 1. DAPT manufacture (single disperser)

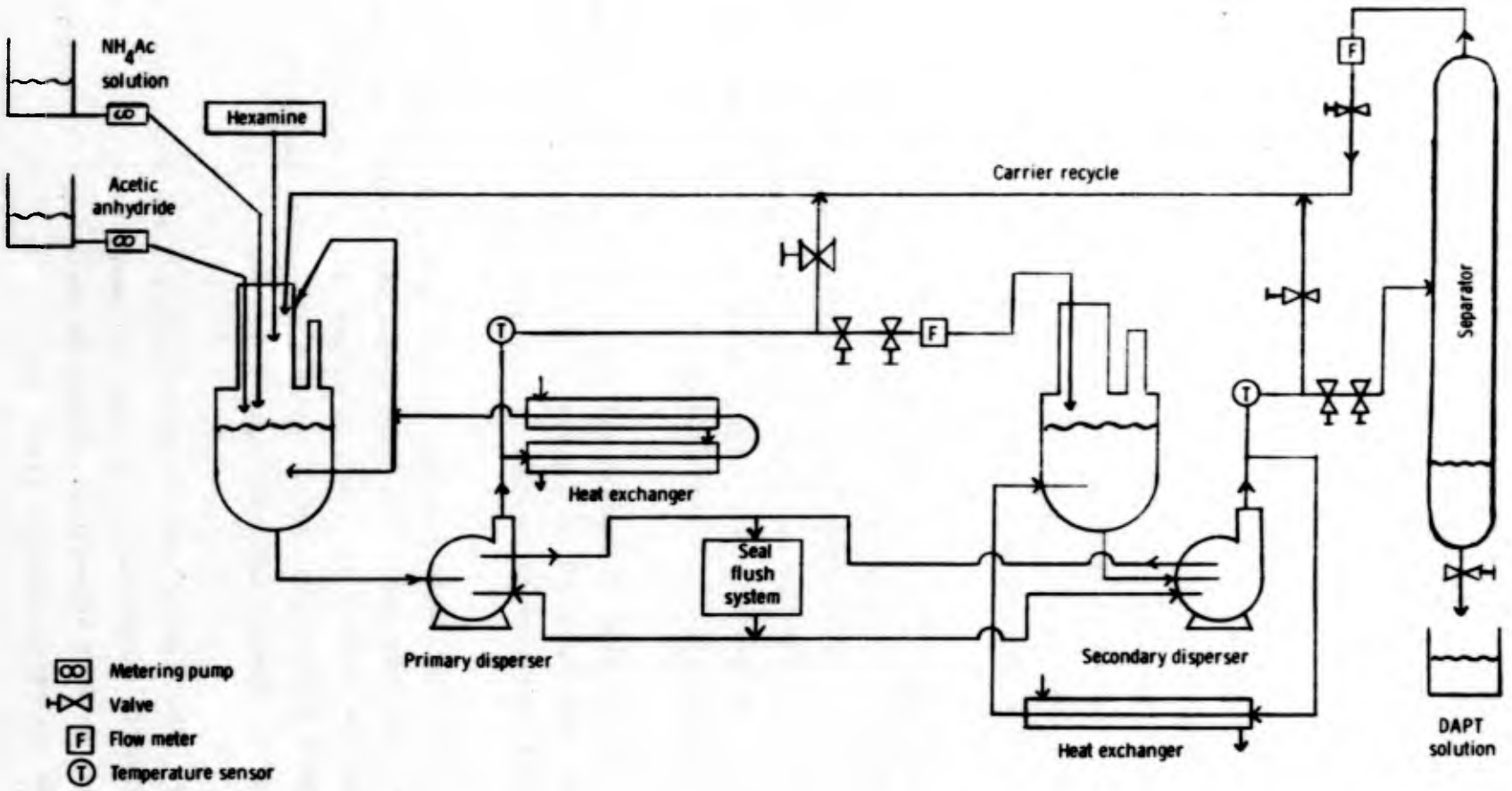


Figure 2. DAPT manufacture (double disperser).

Production Rate - The highest throughput was 45 lb/hr of DAPT in run 13. The maximum production rate for this size equipment is probably several times this rate, and the actual capacity of the ICP equipment for this and the other chemistry steps is still to be established.

Another way to explain the potential for higher production in this small equipment is to consider the recirculating carrier as a liquid belt. The ingredients which are fed onto this belt react, and they then are separated from the belt. The production rate depends primarily on the rate the ingredients are added to the belt. At some maximum addition rate, the overloaded belt will cease to act like a liquid carrier. This is the limit which should be determined in a future program.

Ammonia Addition - The in situ formation of ammonium acetate has a decided economic advantage. Adding the ammonia directly to the disperser results in an unwanted reaction with acetic anhydride to form acetamide. Since the reaction converts the acetic anhydride to acetic acid, one-third of the product was recirculated to the disperser and the ammonia was added in this recirculating stream (Figure 1).

Because the reaction of ammonia and acetic acid is quite exothermic, a heat exchanger was installed in the system immediately downstream of the point of ammonia addition to remove the heat generated.

Arriving at a satisfactory method of feeding NH_3 with limited equipment proved to be quite time consuming. The system which worked best was a precalibrated flow control valve set to deliver close to the desired 14 g/min flow for a known time. Actual ammonia flow rates were confirmed by weight loss of the ammonia cylinder during each run.

Heat Sink - The heat of reaction of Equations 3 and 4 are high, 400 and 160 Btu/lb of DAPT, respectively. Heptane performed excellently as a heat sink, with very uniform temperature control on each run. All temperature control charts are being supplied separately.

Viscosity - The mixture of solid hexamine, acetic anhydride, and ammonium acetate has a very high viscosity. In conventional processing, water is added to reduce the viscosity; with ICP, viscosity is not a problem as the ingredients can be dispersed readily in the carrier as a low viscosity suspension. This allows studies to be made to optimize the amount of water for the reaction with no concern for viscosity problems.

Reaction Time - Reaction time is controlled by the average stay time in the dispersers. If a disperser volume is 10 gal and the flow rate in and out of the disperser is 1 gal/min, the average stay time for materials in the disperser is 10 min. Disperser volume and flow rate are the processing factors which are used to provide the desired reaction time.

Reactant Addition - Ingredients were fed by Zenith gear pumps for the liquids. The GraviMerik belt feeder, with its 5-lb/min capacity, was too large for the 140 g/min hexamine feed rate. Consequently, the hexamine was preweighed into 1/4-min increments and added to the disperser by hand. The disperser design is such that it attenuates the incremental additions so that no measurable surge is found in the process.

Separation - After the reaction is complete, the continuous flow in small diameter pipe from the disperser enters the relatively large cross-section separator. The turbulent flow immediately ceases and the low density carrier separates by gravity, rises, and is recirculated through the system. The product is drawn from the bottom of the separator at a rate which maintains the product/carrier interface at a preselected level. The large difference in density, .69 versus 1.15, results in quite complete separation of the heptane carrier from the aqueous DAPT solution. There was no noticeable carrier loss in CSD operations. If any small amount of heptane is in the DAPT solution it is carried over into the next step and recovered there.

Seal Flush - The seal flush system consists of a separate pump, supply tank, filters, and a heat exchanger. Its function is to supply a continuous flow of clean carrier to the double mechanical seal in the disperser pumps.

This recirculating fluid is supplied to the seal at about 20 psi above the pressure in the pump. This is a safety feature which prevents any potentially hazardous fluid in the pump from leaking into the seal. Any flow through the seal must be from the seal into the pump housing.

Pilot Plant Runs

Nine plant runs were made under this contract (Table 1). (Runs 01 to 04 were previously made under CSD funding.) The most significant run, 13, was the only run made with the dual disperser system (Figure 2). Three runs were made to establish the feasibility of ammonia addition. Four runs were made to study the effect of varying the amounts of water as an ingredient. One run was made to duplicate an earlier run except that throughput was increased 50 percent. At the conclusion of each run the feeders were stopped and the carrier was allowed to recycle for 10 minutes. Essentially all ingredients were recovered, as shown in Table 1, from the material balance figures.

Dual Dispersers - The most significant run, 13, gave a DAPT yield of 109 percent at a throughput of 45 lb/hr of pure DAPT. Run time was 78 min, and 142 lb of 42 percent DAPT solution was produced. Reaction temperature was a steady 25°C. The mole ratios of ingredients duplicated those recommended by Picatinny except that the mole ratio of acetic anhydride was reduced slightly from 2.6 to 2.5.

The first disperser had an average stay time of 20 min while the second disperser average stay time was 10 min. This time was calculated from the respective operating volumes of 20 and 10 gal and a flow rate of 1 gal/min. The calculated concentration of ingredients in suspension in carrier was 1.82 lb/gal.

This run, made months after the previous run, was made primarily to supply a large quantity of DAPT for the nitration to DADN. Because the ammonia feed equipment had been disassembled, it was decided, as a matter of economy of time and dollars, to run with ammonium acetate instead.

TABLE 1. DAPT PILOT PLANT RUNS

Run No.	Time, (min)	Material feed rates, (moles/min)					DAPT/HAc recycle, (g/min)	Material balance		Estimated yield,[a] (percent)	Water, (percent)	Acetic acid, (percent)
		Hexamine	AC_2O	NH_4Ac	NH_3	H_2O		Input, (g)	Output, (g)			
05	16	1.00	2.57	.79	–	4.14	–	8592	8190	87	10.4	32.9
06	16	1.00	2.60	.76	–	3.99	–	8576	8550	87	9.1	36.9
07	16	1.00	2.58	.74	–	3.28	–	8338	8400	88	7.4	37.6
08	16	1.00	2.57	.76	–	2.10	–	8000	7660	96	6.0	39.8
09	0 to 8	1.00	2.58	.79	–	3.86	–					
	8 to 28	1.00	2.58	–	.60	3.92	150	14,236	14,460	99	8.3	34.7
10	0 to 8	1.00	2.48	.87	–	3.61	–					
	8 to 28	1.00	2.48	–	.85	4.38	150	14,315	14,000	95	16.0	32.0
11	0 to 8	1.00	2.54	.77	–	3.99	–					
	8 to 40	1.00	2.54	–	.87	5.25	160	20,935	21,156	94	17.4	30.6
12	16	1.50 (1.00)	3.84 (2.56)	1.14 (.76)	–	5.86 (3.91)	–	12,976	12,370	102	11.8	35.5
13[b]	78	1.50 (1.00)	3.76 (2.51)	1.21 (.81)	–	6.32 (4.21)	–	63,340	64,695	109	12.2	40.4

[a] 120 percent is maximum theoretical

[b] Dual disperser system

NOTE: For runs 12 and 13 (material feed rate columns) the numbers in parentheses give the ingredient ratios based on 1.00 mole of hexamine

Ammonia Addition - In runs 09, 10, and 11, the initial part of the runs was made by feeding ammonium acetate. Once sufficient DAPT solution was accumulated, a matter of 8 min, the ammonium acetate feed was stopped and replaced by ammonia feed and water feed. The schematic for these pilot plant runs is shown in Figure 1.

The first time ammonia was added to the recycled product stream, the solid ammonium acetate severely slowed the flow of the recycle stream. Laboratory studies showed that the amount of water necessary to dissolve the ammonium acetate as it formed had to be at least 3 moles/mole of hexamine. This water was added, together with the recycled DAPT solution, by gear pumps as shown in the schematic.

The longest run, 11, lasted 40 min with no problems.

All three ammonia runs gave reasonably good yields, but not as good as laboratory results. One shortcoming of these runs was their short average stay time of 6 min. The use of the dual disperser system, described above for run 13, provided the necessary reaction time for all the ingredients and gave an excellent yield.

Effect of Water - Runs 05 through 08 were made to determine the effect of water on the yields. While the lower amounts of water gave the higher yields, this study was obviated by the need for at least 3 moles of water/mole of hexamine to dissolve the ammonium acetate formed by the addition of ammonia.

Higher Throughput - Run 12 was a repeat of run 06, but with 50 percent more throughput. Its higher yield, 102 percent instead of 87 percent, indicates that as the maximum capacity of the equipment is approached, the yields increase.

Recovery of DAPT - Data obtained in the DAPT to DADN nitration showed that significant economics might be achieved if the DAPT were isolated from

its acetic acid-water solution before nitration. The presence of the acetic acid in particular required the use of much larger amounts of HNO_3/H_2SO_4 to make DADN. However these advantages are real only if the DAPT recovery is high.

Attempts were made to remove the water and acetic acid by vacuum distillation. The water and most of the acetic acid was removed in about 15 min when 10 g of the DAPT solution was dried in a Rinco evaporator at 50°C and 1- to 2-mm absolute pressure. When the oily residue was cooled and treated with cold acetone, white crystals of DAPT precipitated. The melting point of the crystals was 191°C, the same as pure DAPT, and a yield of 91 percent was obtained. The decomposition under these conditions was low, due to the short exposure time to the elevated temperature.

Low yields were obtained when larger quantities were purified. A number of experiments were tried with different types of equipment. The best recovery was 63 percent in a 12-liter, three-necked flask equipped with a stirrer. At 55°C and 20-mm absolute pressure, constant weight was achieved (weight loss of 33.4 percent) after 6 hr. Acetone was added and the mixture was chilled to 5°C and filtered.

To confirm the effect of time at high temperature on DAPT yield, another Rinco evaporator run was made. After 18 hr at 71°C the recovery was only 23 percent. In addition, it has been found that DAPT solution will decompose, with time, even at ambient temperature. Storage of the solution must be at 0°C.

It is believed that equipment which will flash off the water and acetic acid with minimum exposure time at high temperature can be procured or designed to give a high yield of pure DAPT. A likely candidate is a vacuum spray drier.

Analytical Studies

Each DAPT run was analyzed for DAPT, water, and acetic acid. These results are reported in Table 1. Water was analyzed by the Karl Fischer method and acetic acid was analyzed by titration with .1N NaOH to a phenolphthalein end point.

NMR analysis for DAPT was unreliable. The estimated yields in the table were obtained by nitrating the DAPT solution with HNO_3/H_2SO_4 at a molar ratio of 10/22.5 at 30°C for 30 min. The DADN was recovered by an ice water quench and filtration. These nitrating conditions are known to yield very close to 84-percent DADN. The DAPT yield was back-calculated simply by dividing the overall yield from hexamine to DADN by .84.

NMR was used for DAPT analysis early in the LASL program. At best, this was an indirect and complex method. When attempted at CSD, it was found that the Varian T-60 NMR equipment did not resolve the spectrum well enough to determine the DAPT in solution. An example of an NMR spectrum is shown in Figure 3 for DAPT run 13. The preferred method, developed by Picatinny Arsenal, uses high pressure liquid chromatograph equipment.

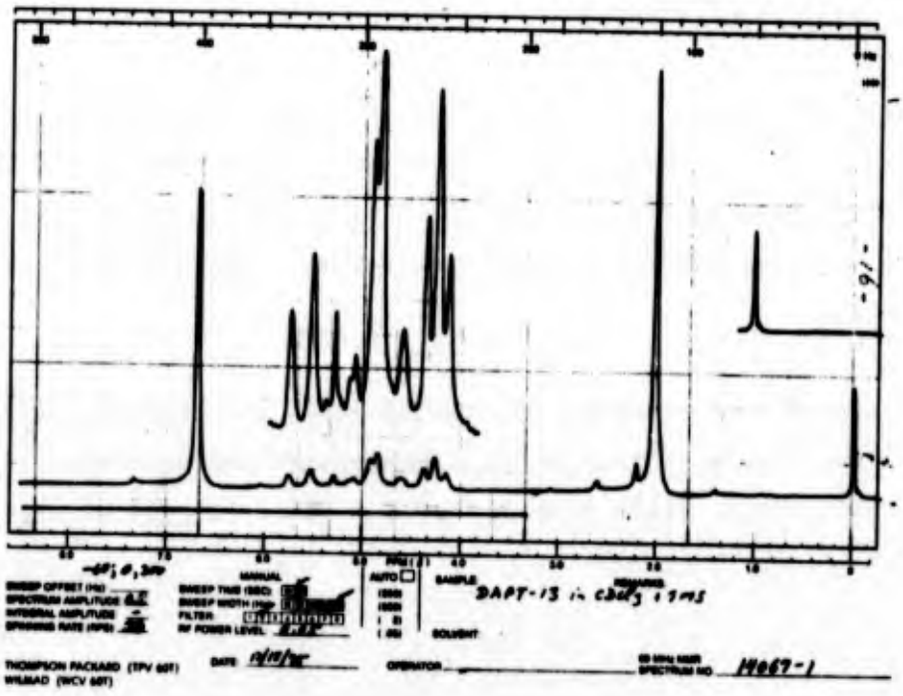


Figure 3. NMR scan of DAPT – pilot plant run 13.

DAPT TO DADN

The second step in the process of making HMX is the nitration of DAPT to DADN by the use of conventional nitrating acids:

DAPT		Nitric acid		Sulfuric acid		DADN		Formaldehyde		Water	
$C_9N_4H_{16}O_2$	+	$2HNO_3$	+	H_2SO_4	⟶	$C_8N_6H_{14}O_6$	+	CH_2O	+	H_2O	(6)
(212)		(63)		(98)		(290)		(30)		(18)	

DADN is 1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane

A side reaction is shown in Equation 7 where DAPT is not completely nitrated. A nitroso group is formed instead of one of the nitro groups. This material, DANNO, is undesirable in the final product because it decreases the yield in the third step, DADN to HMX.

DAPT		Nitric acid		Sulfuric acid		DANNO		Formaldehyde		Water	
$C_9N_4H_{16}O_2$	+	$2HNO_3$	+	H_2SO_4	⟶	$C_8N_6H_{14}O_5$	+	CH_2O	+	H_2O	(7)
(212)		(63)		(98)		(274)		(30)		(18)	

DANNO is 1,5-diacetyl-3-nitro-7-nitroso-1,3,5,7-tetraazacyclooctane

Bench Scale

Fifty-six laboratory nitrations were run to find the best conditions for the operation of the ICP plant. The results are shown in Table 2. The carrier was 99+ mole percent pure heptane. Bench scale equipment consisted of a 1000-ml beaker, an air driven propeller type mixer, a special lid containing built-in baffles for vigorous agitation, a thermometer, and a nitrogen purge. The temperature was controlled with an outside water bath. The first 13 runs used a glass beaker; all the others used a Teflon beaker because of its nonstick properties.

Procedure - Heptane (400-ml) is placed in a beaker and the 98 percent-HNO_3 is added. The sulfuric acid is then added with stirring. A

TABLE 2. DAPT TO DADN PILO

Run No.	Mole ratios				Feed, (g)				
	DAPT	HNO_3	H_2SO_4	Urea	DAPT	DAPT source	HNO_3 (98 percent)	H_2SO_4 (97 percent)	Urea
L-01	1.00	2.92	19.23	.48	15.0	1	4.8	50.2	.75
L-02	1.00	2.92	19.23	.48	15.0	1	4.8	50.2	.75
L-03	1.00	2.92	19.23	–	15.0	1	4.8	50.2	–
L-04	1.00	9.77	19.23	–	15.0	1	16.0	50.2	–
L-05	1.00	6.10	19.23	–	15.0	1	10.0	50.2	–
L-06	1.00	2.92	19.23	–	16.0	2	4.8	50.2	–
L-07	1.00	10.0	20.0	–	10.5	3	31.5	98.0	–
L-08	1.00	10.0	20.0	–	21.0	4	31.5	98.0	–
L-09	1.00	3.00	6.00	–	10.5	3	9.45	29.4	–
L-10	1.00	6.7	13.5	–	5.4	5	8.1	25.2	–
L-11	1.00	6.7	13.5	–	6.9	6	8.1	25.2	–
L-12	1.00	6.7	13.5	–	6.0	7	8.1	25.2	–
L-13	1.00	6.7	13.5	–	10.8	8	8.1	25.2	–
L-14	1.00	6.7	13.5	–	5.4	5	8.1	25.2	–
L-15	1.00	6.6	13.2	–	10.8	5	16.2	50.4	–
L-16	1.00	5.0	10.0	–	5.4	3	8.1	25.2	–
L-17	1.00	5.0	10.0	–	15.0	1	8.1	25.2	–
L-18	1.00	5.0	10.0	–	15.0	1	8.1	25.2	–
L-19	1.00	10.0	20.0	–	5.4	3	16.2	50.4	–
L-20	1.00	10.0	20.0	–	10.8	9	16.2	50.4	–
L-21	1.00	10.0	20.0	–	15.0	1	16.2	50.4	–
L-22	1.00	10.0	20.0	.5	15.0	1	16.2	50.4	.75
L-23	1.00	10.0	20.0	–	5.4	3	16.2	50.4	–
L-24	1.00	10.0	20.0	–	5.4	3	16.2	50.4	–
L-25	1.00	10.0	20.0	–	15.0	1	16.2	50.4	–
L-26	1.00	10.0	20.0	–	15.0	1	16.2	50.4	–
L-27	1.00	10.0	20.0	–	15.0	1	16.2	50.4	–
L-28	1.00	10.0	20.0	–	30.0	1	32.4	100.8	–
L-29	1.00	10.0	11.4	–	15.0	1	16.2	28.0	–
L-30	1.00	10.0	22.0	–	15.0	1	16.2	56.0	–

[a]Mole weight assumed 290

APT TO DADN PILOT PLANT NITRATIONS

SO_4 rcent)	Urea	Quench ratio H_2O/feed	Spent acid/ DADN, (lb)	Reaction temperature, (°C)	Reaction time, (min)	Solids yield, (g)	Yield (moles solid[a]/ moles DAPT), (percent)
.2	.75	2	–	30	15	–	<10
.2	.75	2	210	30	15	1.0	13
.2	–	2	105	30	15	2.0	26
.2	–	2	40	30	15	6.0	80
.2	–	2	41	30	15	5.5	73
.2	–	2	70	30	15	3.0	40
.0	–	2	30	30	15	14.0	95
.0	–	2	30	30	15	10.0	69
.4	–	1	10	30	60	10.C	69
.2	–	2	30	30	15	3.9	71
.2	–	2	30	30	15	4.0	73
.2	–	2	30	30	15	4.0	73
.2	–	2	140	30	15	–	<10
.2	–	2	25	30	15	4.5	82
.4	–	2	25	30	15	9.0	80
.2	–	2	19	40	15	6.0	81
2	–	2	144	30	15	1.0	13
2	–	2	144	30	15	1.0	13
4	–	1	36	30	15	4.0	55
4	–	1	77	30	15	2.0	28
4	–	1	30	30	15	5.5	76
4	.75	1	34	30	15	4.8	66
4	–	2	24	30	15	5.0	70
4	–	2	24	43	15	5.0	70
4	–	1	33	43	15	5.0	70
4	–	1	30	43	30	5.5	76
4	–	1	29	43	45	5.7	78
8	–	1	31	43	15	10.4	73
0	–	2	90	43	15	2.0	28
0	–	1	25	43	15	7.0	96

TABLE 2.

Run No.	Mole ratios				Feed, (g)				
	DAPT	HNO_3	H_2SO_4	Urea	DAPT	DAPT source	HNO_3 (98 percent)	H_2SO_4 (97 percent)	Urea
L-31	1.00	10.0	22.2	–	15.0	1	16.2	56.0	–
L-32	1.00	3.3	22.2	–	15.0	1	5.4	56.0	–
L-33	1.00	5.0	22.2	–	15.0	1	7.9	56.0	–
L-34	1.00	5.0	22.2	–	15.0	10	7.9	56.0	–
L-35	1.00	10.0	22.2	–	15.0	10	16.2	56.0	–
L-36	1.00	10.0	22.2	–	15.0	11	16.2	56.0	–
L-37	1.00	10.0	22.2	–	15.0	12	16.2	56.0	–
L-38	1.00	13.1	15.4	–	5.4	5	16.2	28.7	–
L-39	1.00	10.0	11.4	–	5.4	3	16.2	28.7	–
L-40	1.00	6.1	19.6	–	5.4	3	10.0	50.2	–
L-41	1.00	3.0	6.0	–	10.5	3	9.45	29.4	–
L-42	1.00	4.0	6.0	–	10.5	3	12.6	29.4	–
L-43	1.00	3.0	6.0	–	29.2	11	9.45	29.4	–
L-44	1.00	13.1	15.4	–	4.1	3	16.2	28.7	–
L-45	1.00	2.7	5.4	–	29.2	13	9.45	29.4	–
L-46	1.00	5.2	10.3	–	5.4	3	8.1	25.2	–
L-47	1.00	4.0	6.0	–	10.5	3	12.6	29.4	–
L-48	1.00	10.0	22.8	–	15.0	11	16.2	56.0	–
L-49	1.00	10.0	22.8	–	15.0	11	16.2	56.0	–
L-50	1.00	10.0	22.8	–	15.0	11	16.2	56.0	–
L-51	1.00	8.7	19.3	–	15.0	14	16.2	56.0	–
L-52	1.00	8.7	19.3	–	15.0	14	16.2	56.0	–
L-53	1.00	4.8	19.3	–	15.0	14	9.0	56.0	–
L-54	1.00	4.8	17.2	–	15.0	14	9.0	58.3[d]	–
L-55	1.00	5.4	19.6	–	15.0	14	10.15	61.0[e]	–
L-56	1.00	5.4	19.6	–	15.0	14	10.15	61.0[e]	–

[a] Mole weight assumed 290

[b] Addition time: 0 to 15 min

[c] Addition time: 0 to 15 min and 15-min reaction

[d] 86 percent H_2SO_4

[e] 93 percent H_2SO_4

DAPT Source;

1 DAPT 91011

2 DAPT 91011, concentrated to 6

3 DAPT pure

4 DAPT pure + 100 percent AcOH

5 DAPT pure + 25 percent NH_4Ac

6 DAPT pure + 20 percent NH_4Ac +

7 DAPT pure + 24 percent NH_4Ac +

TABLE 2. (Contd.)

H_2SO_4 (percent)	Urea	Quench ratio H_2O/feed	Spent acid/ DADN, (lb)	Reaction temperature, (°C)	Reaction time, (min)	Solids yield, (g)	Yield (moles solid[a]/ moles DAPT), (percent)
56.0	–	1	30	43	10	5.8	80
56.0	–	1	56	43	15	2.7	37
56.0	–	1	50	43	20	2.7	37
56.0	–	1	48	30	20	3.3	46
56.0	–	1	50	30	20	3.5	48
56.0	–	1	24	30	20	7.2	99
56.0	–	1	83	30	20	2.1	30
28.7	–	1	26	30	15	3.8	69
28.7	–	1	19	30	15	5.9	80
30.2	–	1	22	30	15	5.9	80
29.4	–	1	14	30	15	8.4	58
29.4	–	1	33	30	15	3.2	22
29.4	–	1	175	30	15	.6	4
28.7	–	1	21	30	15	4.7	85
29.4	–	1	226	30	15	.6	4
25.2	–	2	23	30	15	5.1	70
29.4	–	2	17	30	15	9.6	67
26.0	–	1	24	30	20	7.2	99
26.0	–	1	24	30	15[b]	7.2	99
26.0	–	1	24	30	30[c]	7.3	100
26.0	–	1	25	30	20	7.0	81.5
26.0	–	1	24	30	20	7.2	84
26.0	–	1	24	30	20	6.6	77
28.3[d]	–	1	28	30	20	5.8	68
31.0[e]	–	1	32	30	20	5.4	63
31.0[e]	–	1	25	30	20	6.8	79

concentrated to 6 percent H_2O

100 percent AcOH

25 percent NH_4Ac

20 percent NH_4Ac + 22 percent AcOH

24 percent NH_4Ac + 10 percent H_2O

8 DAPT pure + 63 percent NH_4Ac

9 DAPT concentrate: 2.5 percent H_2O + 27.4 percent AcOH

10 DAPT 6: 9.1 percent H_2O, 36.9 percent AcOH

11 DAPT 11: 17.4 percent H_2O, 30.6 percent AcOH

12 DAPT 7: 7.4 percent H_2O, 37.6 percent AcOH

13 DAPT 12: 11.8 percent H_2O, 35.5 percent AcOH

14 DAPT 13: 12.2 percent H_2O, 40.4 percent AcOH

maximum temperature increase of 1°C occurs. The acid/carrier mixture is brought to the desired reaction temperature by a water bath. The DAPT, as a solution or as crystals, is added within a 1- to 2-min period. At this point there is an initial exotherm and cooling is applied by means of the water bath. The reaction is continued at the temperature and reaction time desired. At the end of the reaction the total acid phase (bottom layer) is separated from the heptane and added to ice water. The DADN precipitates, is filtered, given several water washes, weighed, and analyzed.

Aging of DAPT Solution - The plant run in which the DAPT solution was made is shown in Table 2 for each bench scale nitration. The DAPT solution was initially stored at room temperature. After runs L-35 and L-36 the affect of aging on the DAPT solution became apparent. Both runs were made with 1/10/22 molar ratio of DAPT/HNO_3/H_2SO_4. Run L-35, made with the DAPT from run 06, which was stored for about 2 months at 25°C, gave a 48 percent-yield. Run L-36, made with DAPT from run 11, stored at 0°C, gave an excellent yield of 99 percent. Consequently all runs after L-37 were made with DAPT solution stored at 0°C. While pure DAPT did not show any decomposition at room temperature, it was also stored at 0°C.

Molar Ratio HNO_3/H_2SO_4 - The HNO_3/H_2SO_4 molar ratio recommended initially by Picatinny Arsenal was 10/22.5. Further work at Picatinny and LASL showed that a lowering of the HNO_3 was possible. This effect was studied in runs L-52 and L-53. The amounts of 4.8 and 8.7 moles HNO_3 gave much closer yields (77 and 84 percent, respectively) than would be expected from the amounts of acid used. However, lowering of the H_2SO_4 from 19.23 to 11.4 moles resulted in the yield dropping from 80 to 28 percent (compare runs L-04 and L-29).

Some lowering of the amount of nitric acid may be economical, but the sulfuric acid is close to the optimum. This should be further studied by pilot plant runs and an economic evaluation.

Pure DAPT versus DAPT Solution - Purified DAPT was nitrated with much less acid than needed for nitrating the DAPT solution. Instead of a DAPT/HNO_3/H_2SO_4 ratio of 1/10/22, a ratio of 1/5/10 was used to obtain a yield of 81 percent for run L-16. A yield of 82 percent was obtained from run L-14 at a molar ratio of 1/6.6/13.4. When DAPT solutions are nitrated with these low acid ratios, a yield of only 13 percent (runs L-17 and L-18) was obtained.

Similar results are shown with pure DAPT in run L-39 at a ratio of 1/10/11.4 with an 80-percent yield and in run L-29, using DAPT solution 91011, at the same ratio with only a 28-percent yield.

In run L-41, at the very low acid ratio of 1/3/6, a 58-percent yield was obtained while with DAPT solution only a 4-percent yield was obtained at the same DAPT/acid ratio in run L-43.

These illustrations show that higher yields and/or lower acid requirements can be anticipated with purified DAPT. The advantages of less acids are discussed in detail in the CSD economic analysis under "Optimized Process Conditions."

Reaction Temperature - It does not appear that the reaction temperature influences the yield significantly in the range between 30° and 43°C. By comparing laboratory runs 23 and 24 it can be seen that a yield after 15 min at 30°C (70 percent) does not differ from the yield at 43°C (also 70 percent).

Laboratory results from Picatinny Arsenal and LASL show that a reaction time reduction from 20 to 10 min can be obtained at 40° to 45°C.

It was not observed in the above laboratory studies or in CSD laboratory studies that partial decomposition occurs above 35°C. However, decomposition was clearly shown in the pilot plant runs.

Exotherms - Crude DAPT gives a strong exotherm at the beginning of a nitration run. The temperature climbs from 110° to 140°F in 2 min. When pure DAPT is used for the DADN nitration, no exotherm is observed. The nitration is very clean and no brown fumes are produced. When pure DAPT mixed with acetic acid was nitrated, only a slight exotherm was produced. However, nitration of a mixture of pure DAPT, acetic acid, and water gave a very strong exotherm. Consequently, it is believed that the exotherm observed during the first 2 min of nitration is primarly due to the heat of dilution between the water present in the crude DAPT and the sulfuric acid present in the mixed acids.

Another exotherm, observed by LASL at the end of the nitration and thought to be due to the reaction between HNO_3 and formaldehyde, was solved by addition of urea. The nitration in heptane never showed this exotherm and urea did not appear to be needed. Tests were conducted to determine if yields improved by adding urea. A direct comparison can be made of runs 21 and 22 where the presence of urea lowered the yield from 76 to 66 percent on these otherwise identical runs.

Reaction Time - A good indication of the effect of reaction time at 43°C was obtained in laboratory runs 25, 26, and 27. The reaction time for these runs was 15, 30, and 45 min, respectively. The yield increased from 70 to 76 to 78 percent. All runs were made at the same DAPT/HNO_3/H_2SO_4 molar ratio of 1/10/20.

Laboratory run 30 showed an excellent yield (96 percent after a 15-min reaction time while run 31 gave only 80 percent after 10 min. These runs differed from those described in the paragraphs above by a change in the molar ratio of DAPT/HNO_3/H_2SO_4 to 1/10/22.2.

This indicates that the reaction time does not influence the yield very much in the 15- to 20-min range.

Sulfuric Acid Concentration - In recovering the spent mixed acids, sulfuric acid can only be concentrated to 93 percent. Further concentration requires the addition of oleum, which means that the capital outlay for an oleum plant can be avoided if use of 93-percent sulfuric acid does not seriously affect the yield.

No differences were found in the yield when 93-percent H_2SO_4 was used instead of 98 percent. Run L-56 shows a yield of 79 percent with 93-percent H_2SO_4 and a similar yield (77 percent) was obtained in run L-53 with 98 percent-sulfuric acid. A direct comparison was made in pilot plant runs P-09 and P-10 which also show very little difference in yield.

Quenching - The quench ratio is the ratio of the amount of ice water used to precipitate the DADN from the spent acids divided by the total input of ingredients. The advantage of a low quench ratio is that there is less spent acid to fortify, as there is less water to remove. Table 2 shows the pounds of spent acid per pound of DADN for each run made. On the average about 20 to 30 lb of spent acid is produced per pound of DADN.

Pilot Plant

Data for the nine pilot plant runs made are given in Table 3. A single disperser system was used for runs P-02 through P-08 (Figure 4); a double disperser system was installed for runs P-09 and P-10 (Figure 5).

Single Disperser System - The sulfuric acid and nitric acid were premixed to eliminate the heat of the solution between two acids in the DAPT-DADN nitration. This was easily done by using the ICP disperser filled with heptane. The temperature of the heptane was 15°C, and H_2SO_4 was poured directly into the disperser while the heptane circulated. The HNO_3 then was metered into the disperser at about .2 gal/min. The mixture was collected in the mixed acid run tank and stored until the run started.

The heptane level was set at 18 gal, and the temperature was controlled at 30°C for the total sytem. Mixed acids and the DAPT solution were fed

TABLE 3. DAPT TO DADN PILOT PLANT NITRATIONS

Run No.	Mole ratios				Feed rates, (g/min)				Quench Ratio: H_2O/feed	Reaction temperature, (°C)	Reaction time, (min)	Run time, (min)	Yield, (g)	Yield, (moles solid[b]/ mole DAPT), (percent)
	DAPT	HNO_3	H_2SO_4	Urea	DAPT	HNO_3 (98 percent)	H_2SO_4 (97 percent)	Urea						
P-02	1.00	2.95	20.20	.50	327(1)	106	1140	17	.64	30	10	17[a]	–	–
P-03	1.00	2.96	19.70	.49	298(2)	98	1015	15	1.03	30	10	28	538	13
P-04	1.00	2.96	19.20	.50	175(2)	56	582	9	2.0	30	20	26	634	28
P-05	1.00	5.81	18.70	.51	181(2)	115	582	9.6	2.0	30	20	34	1900	62
P-06	1.00	5.62	18.47	.51	161(3)	111	575	9.6	2.0	30	20	34	1420	47
P-07	1.00	10.00	22.50	–	175(2)	193	682	–	1.0	43	15	44	224	6
P-08	1.00	10.00	22.50	–	177(4)	189	662	–	2.0	30	15	30	235	9
P-09	1.00	6.35	23.0	–	154(5)	120	680	–	–	28	30[c]	60	3873	79.8[d]
P-10	1.00	6.45	22.7	–	154(5)	121	695[e]	–	1.6	26	30[c]	160	11,063	85.5[d]

Notes:
[a] One gear pump feeder stopped; run aborted
[b] Mole weight assumed 290
[c] Series dispersers - 20 min first and 10 min second
[d] Calculated from hexamine to DADN
[e] H_2SO_4 - 93 percent

DAPT Source:
(1) DAPT run 5
(2) DAPT 91011: 13.6 percent H_2O, 31.76 percent AcOH
(3) DAPT run 8: 6.0 percent H_2O, 38 percent AcOH
(4) DAPT run 6: 9.1 percent H_2O, 36.9 percent AcOH
(5) DAPT run 13: 12.2 percent H_2O, 40.4 percent AcOH

into the disperser by gear pumps. When urea was used in the reaction, it was dissolved in the DAPT solution. After 10 min of feeding, the total volume in the disperser was 20 gal. At that time valve B was opened to a rate of 2 gal/min controlled by valve C and carrier returned. The ratio of this flow rate to the total volume in the disperser gives an average stay time of 10 min.

A much higher ratio of ingredients to carrier can be used in the present size equipment to give a significantly higher production rate. These runs were limited by the small cooling capacity of the existing heat exchangers.

Foaming occurred during the nitration due to the evolution of formaldehyde. While foaming may cause problems in conventional reactors, a good flow of return carrier into the disperser depressed the foaming so that it created no problems. The DADN spent acid solution was taken off from the

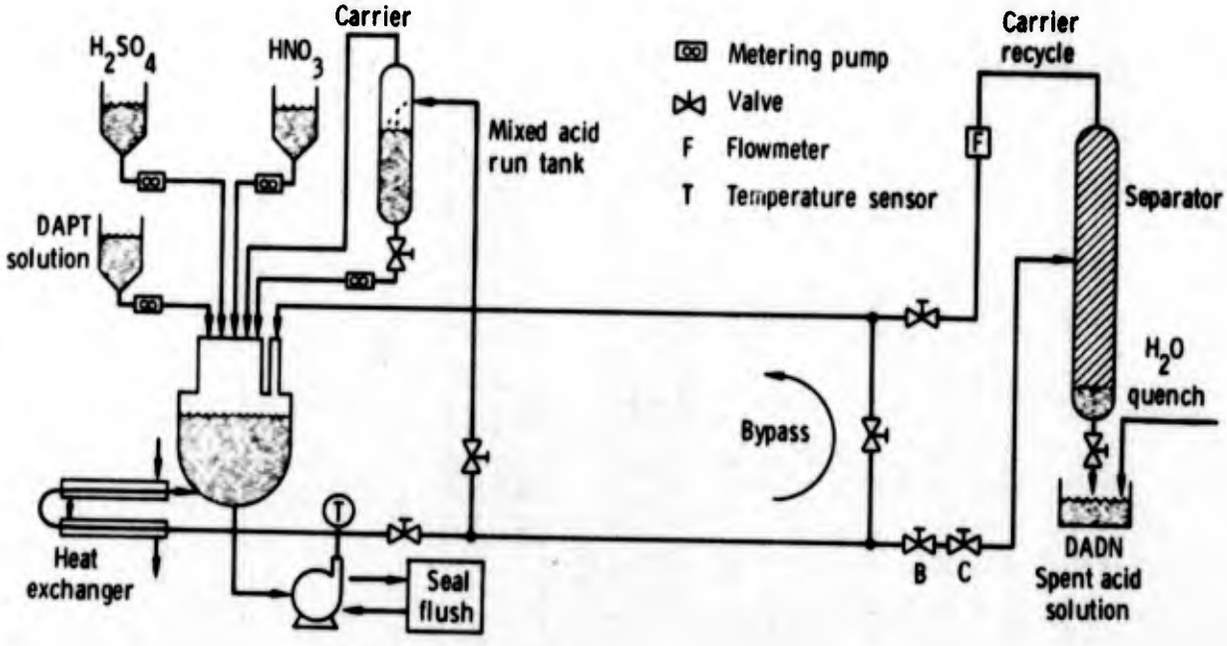


Figure 4. DADN manufacture (single disperser).

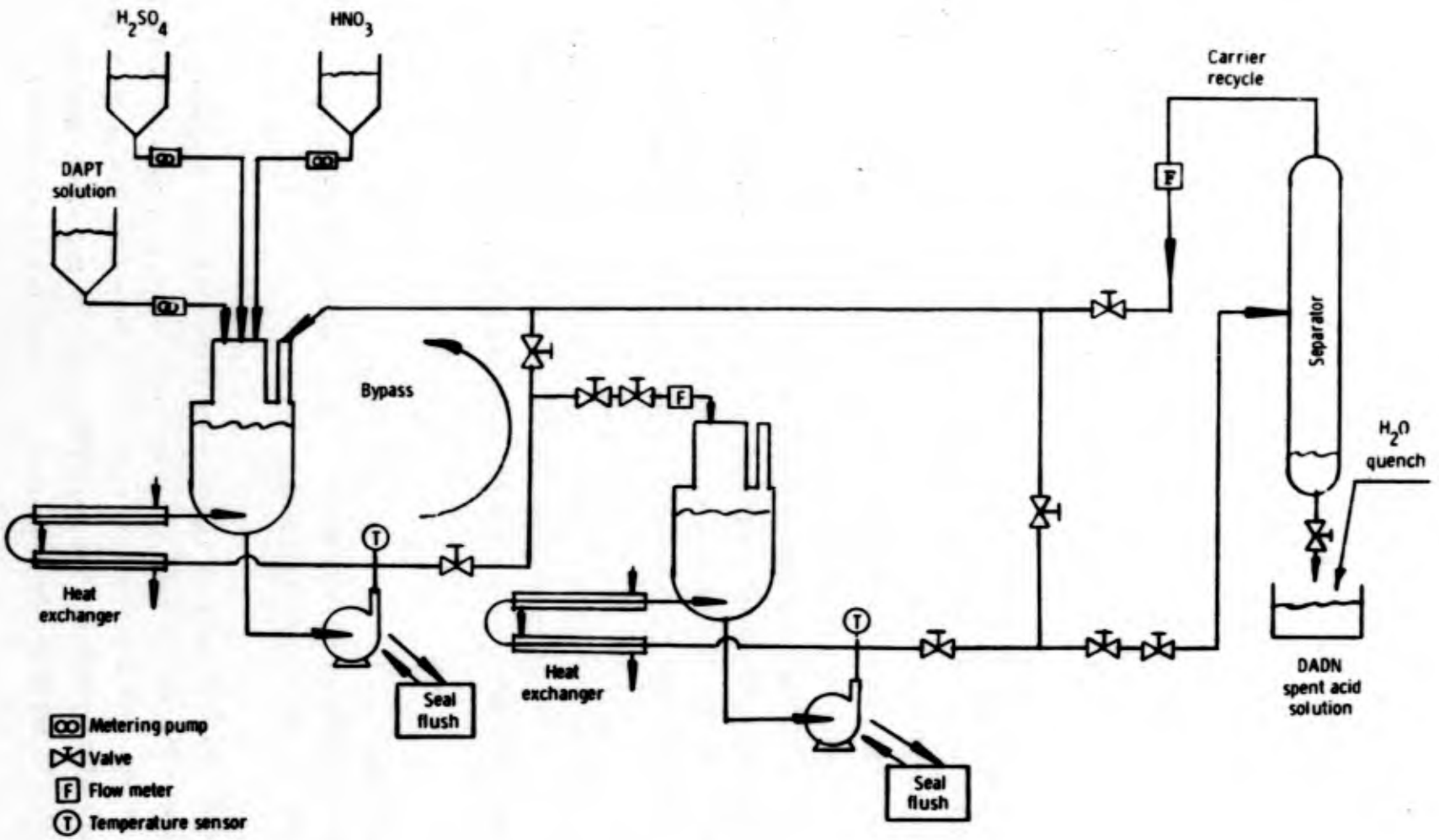


Figure 5. DADN manufacture (double disperser).

separator into a stainless steel drum containing ice water. The temperature was kept below 30°C and stored several hours before filtration of the DADN. Most spent acid was removed easily from the bottom of the drum because DADN floats. The DADN was given several cold and hot water washes and dried in a vacuum oven at 75°C.

Variables which were investigated in the single disperser system were: (1) molar ratio of DAPT/HNO_3/H_2SO_4, (2) reaction time, and (3) reaction temperature.

Double Disperser System - After the low yield of run P-05 and its high DANNO content of 25 percent (see Analytical Studies), the pilot plant was rebuilt to the dual disperser configuration. This prevents partially reacted material like DANNO from leaving the process. Due to the longer reaction time with two dispersers, the reaction temperature could be dropped. This is important because the maximum temperature should be 30°C. While laboratory data showed a maximum operating temperature of 43°C before decomposition occurs, the data from the pilot plant runs revealed decomposition at temperatures over 35°C (described in the next section).

HNO_3 and H_2SO_4 were added directly to the first disperser because the heat of mixing could be handled by the two dispersers. Addition of urea to the DAPT solution was eliminated because no advantages were found by its presence.

Pilot Plant Runs

The use of decomposed DAPT on the initial runs, up through run P-08, accounts for the low yields obtained.

Runs P-02 and P-03 were designed as baseline runs with standard conditions of 30°C and a 10-min reaction time. The yield was low, only 13 percent. In run P-04 the reaction time was increased to 20 min which gave a higher yield of 28 percent. The DAPT/HNO_3/H_2SO_4 in the above runs was 1/2.96/20.0. To increase the yield, run P-05 was run at a ratio of

1/5.81/18.70 which resulted in a yield of 62 percent. The effect of water on this nitration was studied in run P-06 where DAPT from run 08 with only 6-percent water was used. The conditions were identical to those of run P-05, but the yield dropped to 47 percent.

Runs P-07 and P-08, with the high DAPT/HNO_3/H_2SO_4 ratio (1/10/22.50) showed very low yields. The ICP pilot plant glass separator allowed the observation of some decomposition which was not observed in the laboratory. At the 43°C reaction temperature from run P-07, a decomposition occurred which produced gases that stayed in the product layer as small bubbles. As the bubbles accumulated they created a low apparent density in the top of the product layer. This resulted in "globs" of the product layer breaking off and rising through the heptane layer. This was not observed when the reaction temperature was below 35°C. Consequently, the remaining runs were made at temperatures of 30°C or less.

Runs P-09 and P-10 were made to produce enough DADN of high quality for the next chemical step, DADN to HMX. Both experiments ran smoothly. In run P-10 the quench ratio for the product was close to 1/1 but, because of lack of cooling at the end of the run, extra ice water had to be added. The final ratio was 1.6/1.

A sample of the quench solution from run P-10 was analyzed. The result, given in Appendix B, was interpreted and used in the economic analysis of this contract.

It is very obvious that run P-10 was the best run of the DADN series. It lasted almost 3 hr and produced high quality material. The total production was 25 lb; the DADN production rate was 10 lb/hr with a purity of 99 percent; 93-percent H_2SO_4 was used.

Several reasons for the good performance of this run are:

A. The DAPT solution from run 13 was stored at 0°C to prevent decomposition and used as quickly as possible for the nitration.

B. Reaction temperature was dropped to 26°C and no decomposition occurred during the run.

C. The double disperser was used with an average stay time of 20 min in the first disperser and 10 min in the second disperser.

Analytical Studies

Nuclear Magnetic Resonance - Initial analysis was done by NMR because CSD's new HPLC equipment was not operational. DADN is insoluble in DMSO (the solvent for NMR analysis) at ambient temperature. At 100°C only 1-percent DADN dissolves, which makes the interpretation of a DADN NMR spectrum difficult.

The NMR spectra of pilot plant runs P-05 and P-10 are shown in Figures 6 and 7. The spectrum of run P-05 shows extra peaks at 309 and 319 Hz. These peaks are due to the presence of DANNO. Run P-10, made in the double disperser, is completely free of these peaks.

Accurate quantitative determination was impossible by NMR and at that time it was estimated that run P-05 contained 5-percent DANNO. Later, with the HPLC, the percentage of DANNO was 25 percent. However, HPLC confirmed that there was no measurable amount of DANNO in run P-10.

HPLC - Equipment for this modern analytical technique was procured by CSD for this program. A method for the HPLC analysis of DADN, DANNO, SEX, and HMX was developed at Picatinny Arsenal and is used by CSD with minor changes in the solvent system.

DADN, DANNO, SEX, and HMX standard samples were supplied by Picatinny. Samples of DADN from runs P-05 and P-10 were analyzed both at Picatinny and at CSD. HPLC scans of runs P-05 and P-10 are shown in Figures 8 and 9. The results from the two facilities were in very close agreement and within the

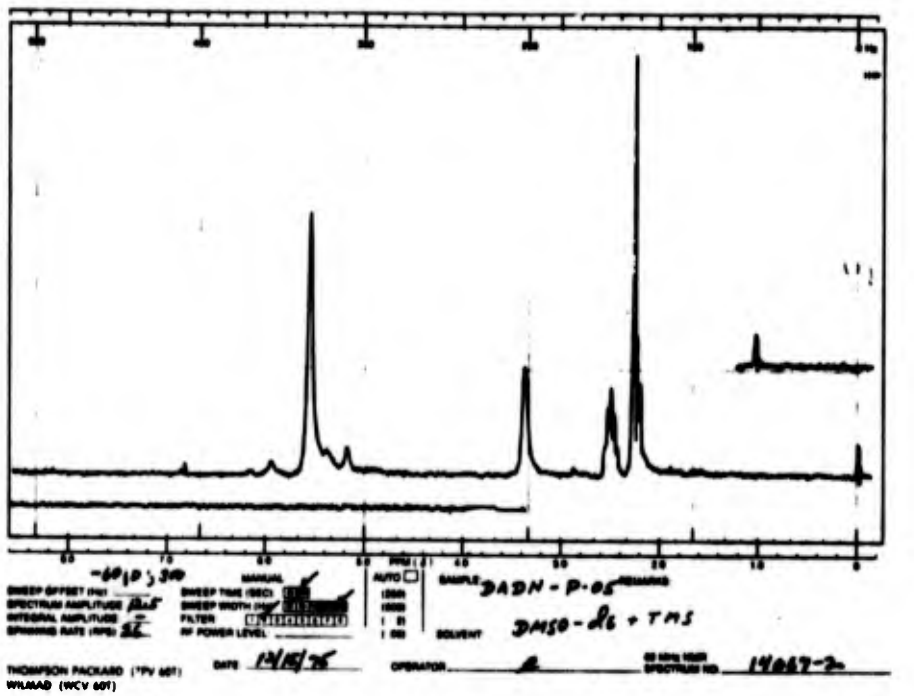


Figure 6. NMR scan of DADN – pilot plant run P-05.

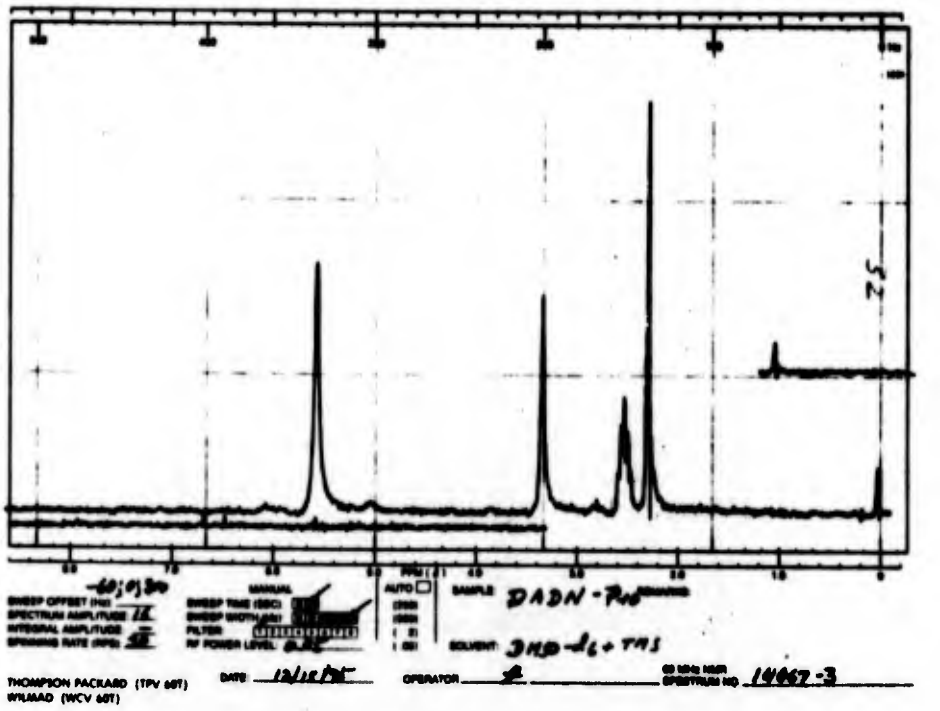


Figure 7. NMR scan of DADN – pilot plant run P-10.

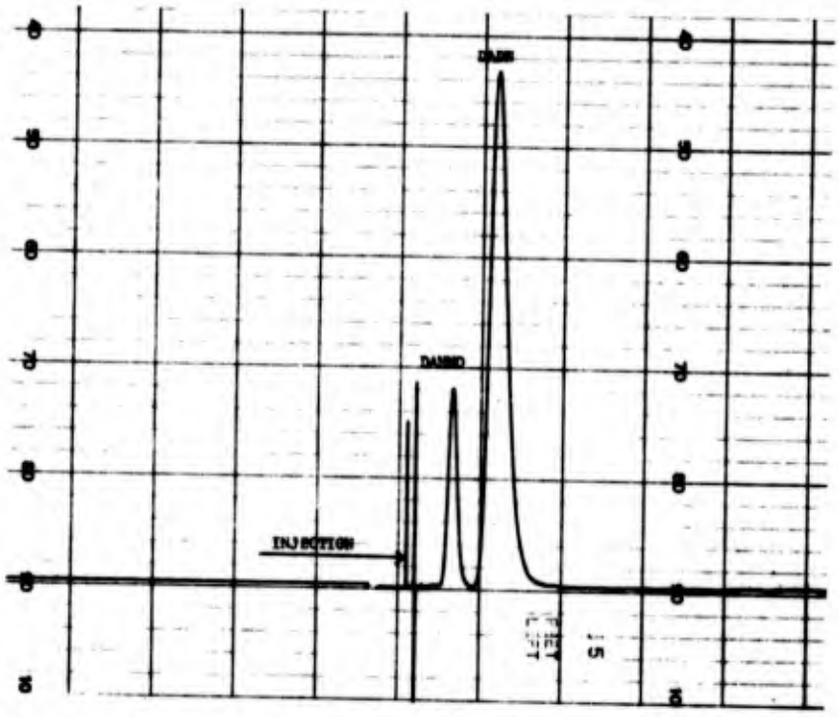


Figure 8. HPLC scan of DADN – pilot plant run P-05.

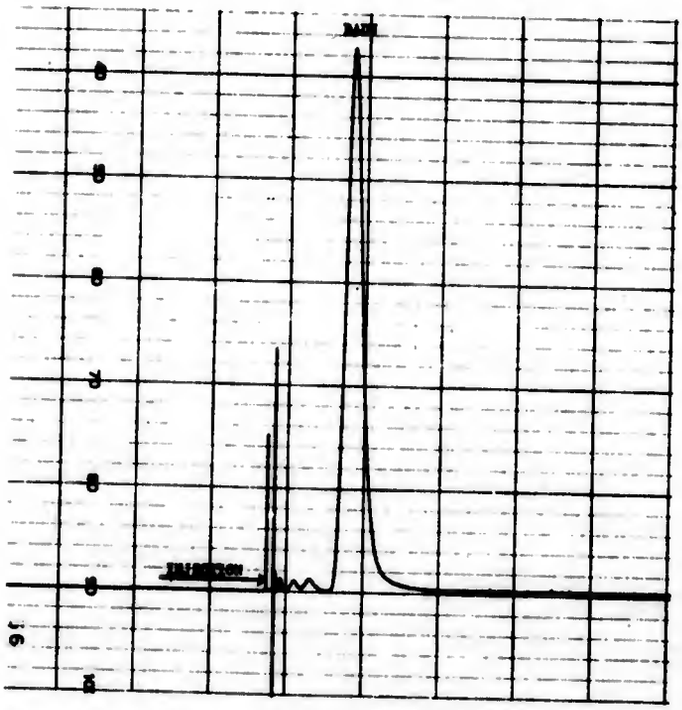


Figure 9. HPLC scan of DADN – pilot plant run P-10.

accuracy of the equipment. A complete description of the HPLC methods used is in Appendix A.

Infrared - Figure 10 shows an infrared spectrum of DADN made in run P-10.

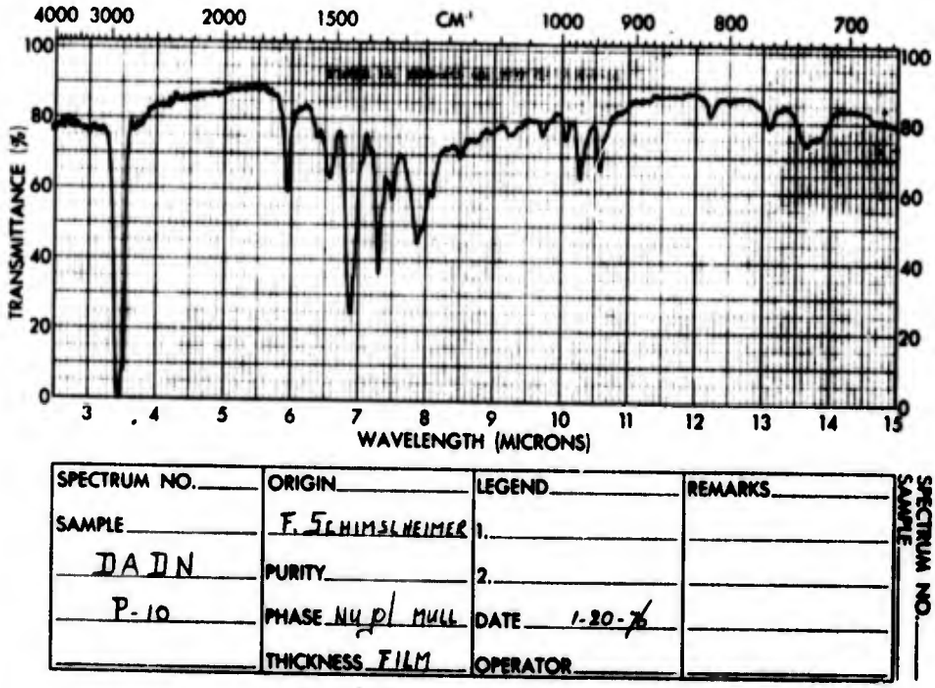


Figure 10. Infrared analysis of DADN - run P-10.

DADN TO HMX

The step from DADN to HMX is to produce HMX by the nitrolysis of DADN with the mixture of PPA/HNO_3. In this nitrolysis one acetyl group in the DADN is replaced by $-NO_2$ according to Equation 8, forming the intermediate SEX.

$$\underset{(290)}{\text{DADN } C_8N_6H_{14}O_6} + \underset{(63)}{\text{Nitric acid } HNO_3} \xrightarrow{\text{PPA}} \underset{(293)}{\text{SEX } C_6H_{11}N_7O_7} + \underset{(60)}{\text{Acetic acid AcOH}}$$

The second acetyl group is then relaced by $-NO_2$ to form the final product, HMX, Equation 9.

$$\underset{(293)}{\text{SEX } C_6H_{11}N_7O_7} + \underset{(63)}{\text{Nitric acid } HNO_3} \xrightarrow{\text{PPA}} \underset{(296)}{\text{HMX } C_4H_8N_8O_8} + \underset{(60)}{\text{Acetic acid AcOH}}$$

PPA is polyphosphoric acid

SEX is 1,3,5-trinitro-7-acetyl, 1,3,5,7 tetraazacylooctane

HMX is 1,3,5,7-tetranitro-1,3,5,7 tetraazacylooctane

Previous work at SRI and Picatinny Arsenal showed that a 65°C reaction temperature for 60 min an 80-percent yield was obtained with these amounts of reactants:

DADN	3.0 g
HNO_3 (99+ percent)	22 g
PPA (115 percent)	56 g

The yield was typically 2.45 g, or 80 percent. The HMX from the reaction is formed as the alpha polymorph.

CSD's task was to adapt this reaction to the ICP pilot plant. Bench scale studies were first made to identify a suitable carrier and the best operating conditions for the plant. The bench scale equipment was modified to permit operation as a closed system to minimize HNO_3 loss and low boiling carrier loss.

Bench Scale

Four separate pieces of equipment were used as reactors:

Reactor A: A 1000-ml Teflon beaker with a high speed stirrer and stainless steel baffles. This was the same unit used for the DAPT-DADN nitration. The Teflon top had openings for the addition of the reactants but was not vapor tight.

Reactor B: A modification of reactor A. The lid permitted a gas tight fit with the Teflon beaker, and an internal stainless steel condenser minimized the buildup of pressure.

Reactor C: A high pressure Berghof autoclave with a stirrer and temperature control. The temperature sensor was located at the top of the autoclave where it measured vapor, rather than liquid, temperature. This drawback could be overcome by laying the autoclave on its side when temperature measurements were desired. The magnetic drive stirrer was Teflon coated and its maximum speed was 1500 rpm.

Reactor D: A resin flask unit with interchangeable 100, 200, and 250-ml bodies. It included a stirrer, condenser, thermometer, and ports for ingredient addition. A cold trap was placed at the condenser exit to prevent the escape of any nitric acid or carrier vapors.

The procedure used the following reactants: (1) DADN from run P-10, (2) HNO_3 (98.7 percent), and (3) PPA (114.8 percent).

All equipment was dried before use. PPA was added to a reactor at 35°C followed by the addition of nitric acid and carrier. Heat was applied, and at the desired reaction temperature solid DADN was added and the reactor was closed.

No exotherms were observed. The reaction media were cooled to 40°C after the desired reaction time. The product is precipitated in water to hydrolyze the PPA and to recover HMX. The nitrolysis produces HMX of a very high purity (99+ percent) in the alpha form. The data are reported in Table 4.

Carrier Study - Bench scale runs were made to compare the yields of reactions in various carriers with the standard procedure without carrier. The carriers investigated were carbon tetrachloride, nitroethane, nitromethane, and fluorinerts.[a]

Runs 110, 111, and 147 were made without carrier to duplicate Picatiny Arsenal experiments. Run 110 is identical to Picatinny's and gave the same result. Run 147 was designed to determine whether DADN dissolved in HNO_3 could be used as a feed material without deleterious effects on the nitration. This would provide a simple solution to the problem of feeding DADN into a pressure reactor with existing feed equipment. The yield was 62 percent as compared with 77 percent. The lowered yield that results when a nitric acid solution of DADN is used has been confirmed by Picatinny. However, the yield was high enough to justify using the HNO_3 solution of DADN for the pilot plant runs.

Carbon Tetrachloride - This carrier was proposed for its "inertness" as compared with heptane. Previous experiments under the CSD-funded program had shown that heptane was nitrated by the HNO_3-PPA mixture at 65°C. CCl_4 was shown to be inert to the reaction mixture but its boiling point of 76°C, so close to the reaction temperature, was of concern.

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[a]Trade name for the 3M Company fluorocarbons.

TABLE 4. BENCH SCALE NITROLYSIS OF DADN

Run No.	Reactants, (g) DADN	HNO_3	PPA	Carrier, (ml)	Carrier, Type	Reactor type[a]	Reaction temperature, (°C)	Reaction time, (min)	Product weight,[b] (g)	Prod yie (per
100	6.0	22.0	56.0	400	CCl_4	A	62	30	–	
101	2.9	22.0	56.0	400	CCl_4	A	62	60	2.3	7
102	2.9	22.0	56.0	400	CCl_4	A	62	90	1.3	4
103	2.9	22.0	56.0	400	CCl_4	A	64	120	1.9	6
104	4.64	17.6	44.8	400	CCl_4	A	65	60	3.3	6
105	4.64	17.6	44.8	400	CCl_4	A	65	90	3.3	6
106	4.64	17.6	44.8	400	FC-48	A	65	60	4.0	8
107	4.64	17.6	44.8	400	FC-48	A	75	60	4.0	4
108	4.64	17.6	44.8	400	FC-48	A	65	90	3.3	6
109	4.64	17.6	44.8	400	CCl_4	A	65	60	3.5	7
110	2.9	22.0	56.0	–	–	D	65	75	2.3	7
111	6.0	22.0	56.0	–	–	D	65	60	3.3	5
112	6.0	22.0	56.0	47	$C_2H_5NO_2$	D	65	60	3.0	4
113	6.0	22.0	56.0	47	CCl_4	D	65	60	4.0	6
114	6.0	22.0	56.0	47	FC-48	D	65	60	3.6	5
115	6.0	22.0	56.0	47	$C_2H_5NO_2$	D	65	60	3.3	5
116	6.0	22.0	56.0	67	$C_2H_5NO_2$	D	65	60	3.5	5
117	6.0	22.0	56.0	67	$C_2H_5NO_2$	D	65	60	3.5	5
118	6.0	22.0	56.0	67	$C_2H_5NO_2$	D	65	60	2.0	3
119	6.0	22.0	56.0	47	FC-77	D	65	60	3.7	6
120	6.0	22.0	56.0	47	FC-77	D	65	60	3.8	6
121	6.0	22.0	56.0	400	CCl_4	B	65	60	4.5	7
122	6.0	22.0	56.0	47	FC-48	D	65	60	3.8	6
123	6.0	22.0	56.0	400	CCl_4	B	62	60	5.3	8
124	6.0	22.0	56.0	400	CCl_4	B	62	60	4.7	7

NITROLYSIS OF DADN TO HMX

2

on	Product weight,[b] (g)	Product yield,[b] (percent)	HPLC analysis HMX	SEX	DADN	Remarks
	–	–	–	–	–	Trial run
	2.3	77.7	–	–	–	
	1.3	43.9	–	–	–	
	1.9	64.2	–	–	–	
	3.3	69.7	9	40	49	
	3.3	69.7	–	–	–	
	4.0	84.5	7	37	55	
	4.0	48.6	–	–	–	
	3.3	69.7	–	–	–	Technical grade CCl_4
	3.5	73.9	–	–	–	
	2.3	77.7	99	.5	.5	
	3.3	53.9	99	.5	.5	Lost product in quench
	3.0	49.0	10	41	49	
	4.0	65.3	29	50	21	
	3.6	58.8	85	14	1	
	3.3	53.9	6	40	54	
	3.5	57.1	–	–	–	
	3.5	57.1	6	18	76	Carrier from run 116
	2.0	32.6	29	31	40	Carrier from run 117
	3.7	60.4	91	9	0	
	3.8	62.0	–	–	–	
	4.5	73.4	21	45	34	
	3.8	62.0	94	6	0	
	5.3	86.5	28	41	31	
	4.7	76.7	19	45	35	

TABLE 4. (Co

Run No.	Reactants, (g) DADN	HNO_3	PPA	Carrier, (ml)	Type	Reactor type[a]	Reaction temperature, (^oC)	Reaction time, (min)	Product weight,[b] (g)	Produ yiel (perc
125	6.0	22.0	56.0	400	CCl_4	C	90	60	0	
126	6.0	22.0	56.0	400	CCl_4	C	70	60	5.0	81
127	6.0	22.0	56.0	400	CCl_4	B	60	60	5.5	89
128	6.0	22.0	56.0	400	FC-48	B	65	60	4.5	7
129	6.0	22.0	56.0	400	FC-48	B	50	60	5.8	94
130	6.0	22.0	56.0	400	CH_3NO_2	B	65	60	4.5	7
131	6.0	22.0	56.0	400	FC-48	B	65	60	4.8	78
132	6.0	26.4	67.2	400	CCl_4	B	62	60	4.9	79
133	6.0	22.0	56.0	400	CCl_4	B	60	120	4.3	70
134	6.0	22.0	56.0	47	CH_3NO_2	D	60	60	3.3	5
135	6.0	22.0	56.0	400	CH_3NO_2	B	65	60	3.8	62
136	4.0	14.7	37.3	267	CCl_4	D	65	60	3.1	50
137	6.0	22.0	56.0	250	FC-48	D	65	60	3.8	62
138	6.0	22.0	56.0	250	CH_3NO_2	D	68	60	4.0	65
139	6.0	22.0	56.0	160	FC-77	D	65	60	3.9	63
140	6.0	22.0	56.0	400	FC-48	B	65	60	5.1	83
141	6.0[c]	22.0	56.0	250	CH_3NO_2	D	65	60	5.0	81
142	6.0	22.0	56.0	250	FC-48	D	75	60	2.7	44
143	12.0	44.0	112.0	95	FC-48	B	65	60	8.4	68
144	12.0	+8.8 44.0	+23.0 112.0	94	FC-48	B	65	60	8.5	69
145	12.0[c]	44.0	112.0	94	FC-48	B	65	60	6.5	53
146	6.0	220.0	56.0	47	FC-48	B	65	60	0	
147	6.0[c]	22.0	56.0	—	—	D	65	60	3.8	62
148	6.0[c]	22.0	56.0	47	FC-40	D	65	60	3.8	62
149	6.0[c]	22.0	56.0	47	FC-40	D	65	60	4.0	65

[a] See procedure in step III.

[b] Assume molecular weight 296 (molecular weight for HMX) to calculate the percent of crude yield.

[c] DADN dissolved in HNO_3.

TABLE 4. (Contd.)

Product weight,[b] (g)	Product yield,[b] (percent)	HPLC analysis HMX	SEX	DADN	Remarks
0	0	—	—	—	
5.0	81.7	15	53	32	
5.5	89.7	20	28	48	
4.5	73.4	26	43	31	
5.8	94.7	4	39	57	
4.5	73.4	0	30	70	
4.8	78.3	36	59	13	80 percent ($PPA+HNO_3$) start; 20 percent at 40 min
4.9	79.9	9	53	37	100 percent ($PPA+HNO_3$) start; 20 percent extra at 40 min
4.3	70.8	14	50	35	
3.3	53.9	77	22	1	.8 g product from CH_3NO_2
		15	45	40	2.5 g product from acids
3.8	62.0	1	11	88	
3.1	50.7	18	51	31	
3.8	62.0	43	45	11	
4.0	65.4	11	16	67	
3.9	63.7	48	43	9	
5.1	83.3	18	56	24	
5.0	81.6	2	17	81	
2.7	44.1	65	30	5	
8.4	68.6	44	48	7	20 percent extra ($PPA+HNO_3$) at 40 min
8.5	69.4	43	46	9	
6.5	53.1	73	24	3	
0	0	—	—	—	
3.8	62.0	97	3	—	
3.8	62.0	77	21	2	
4.0	65.4	70	27	3	

Experiments in reactor B (closed) improved this conversion remarkably (run 123). The yield was 86.5 percent of crude product containing 28-percent HMX, 41-percent SEX, and 31-percent unreacted DADN.

Reactor C, the autoclave, is a tightly closed, high pressure unit. The first experiment (run 125) was run with the previously mentioned poor temperature controller and it was not possible to keep the temperature at 65°C. The reaction was run at around 90°±10°C and produced, after about 20-min reaction time, a sudden pressure increase from 20 to 200 psi. After quenching the reaction products with water, no insoluble materials were obtained. All materials of interest had been decomposed.

With an improved temperature controller, the reaction was run at 70°C (run 126) and shows close to the same result as run 123 which was made in a closed Teflon beker.

Nitroethane and Nitromethane - The solubility of HNO_3 in these liquids is high. However, it was thought that they might be useful as a carrier when saturated with HNO_3. Runs 115, 116, 117, and 118 are a series using nitroethane. Each run used the carrier from the previous run to approach the equilibrium operating solution of HNO_3. The conversion was low and it is believed that the carrier reacted with the PPA/HNO_3. The same effect was observed with nitromethane in runs 130, 134, 135, and 141.

Fluorinerts - The original idea of using Freons in this nitrolysis ran into problems when Freon 112, with a boiling point of 90°C, was no longer available. A search for high boiling fluorocarbons led to 3M fluorinerts (low molecular weight polymers with low viscosity). As they contain no C-H bonds they are not attacked by the PPA/HNO_3 mixture.

Three fluorinerts were used: FC-77, FC-40, and FC-48 with boiling points of 97°, 155°, and 174°C, respectively.

Run 122 with FC-48 at a carrier-to-reactant ratio of 1/1 showed that the fluorinerts would be well suited as inert carriers. At a higher dilution

(run 128) the conversion of DADN to HMX dropped off drastically, presumably because N_2O_5 production by the PPA/HNO_3 was reduced as described in the next section. The two other fluorinerts behaved the same as FC-48.

The fluorinerts and the reacted mixture have about the same density and are difficult to separate. However, when the separation step is made after the water quench, excellent separation is obtained.

Quenching takes place at room temperature at a ratio of 1/1. The product is precipitated out, filtered, washed with cold and hot water several times, and then dried.

Reaction Variables - Variables which would affect the reaction in the pilot plant were studied on the bench scale. These variables included reaction temperature and time and the effect of adding PPA/HNO_3 during the reaction. With CSD's existing equipment the solid DADN could not be added to the pressurized pilot plant. Consequently, it was important to determine the effect on the reaction of using DADN dissolved in HNO_3.

The low yields obtained in these experiments seemed to indicate the carrier was interfering with the reaction (something CSD had not experienced before). Recent data from Picatinny showed that it was important to premix the PPA and HNO_3 before adding the DADN. It is believed that the carrier was interfering with the generation of N_2O_5 which is made more effective by this premixing. By feeding the premixed acids in the third step the low yields shown in the data below should be improved. However, the relative yields are believed valid for the comparison made.

Reaction Temperature - Using FC-48 carrier, the effect of temperature is shown as follows:

Run No.	Temperature, (°C)	Reaction time, (min)	Crude yield, (percent)	Purity, (percent)	HMX yield, (percent)
129	50	60	94.7	4	3.8
128	65	60	73.4	43	26.7
142	75	60	44.1	65	28.7

Little yield improvement is shown at 75°C. To keep the pressure low in the closed system, 65°C appears to be optimum for a 60-min reaction time.

Reaction Time - Two runs were made with all conditions constant except reaction time.

Run 123 for 60 min - crude yield, 86.5 percent; purity, 28 percent
Run 133 for 120 min - crude yield, 70.8 percent; purity, 14 percent

These yield figures show that a longer reaction time decreased the conversion, probably due to decomposition of the product. Since no improvement was obtained with increased time, there was no reason to vary from Picatinny's established 60 min.

Extra Addition of PPA/HNO_3 - Before CSD learned of the need to premix PPA and HNO_3, it was hoped that extra addition of PPA/HNO_3 during the reaction would improve the yield:

Run No.	Carrier	PPA + HNO_3 at start, (percent)	Addition at 40 min, (percent)	Crude yield, (percent)	Purity, (percent)	HMX yield, (percent)
131	FC-48	80	20	78.3	36	28.2
132	CCl_4	100	20	79.9	9	7.9
143	FC-48	100	20	68.6	44	30.2

These yield figures do not show any improvement of the yield.

DADN Dissolved in HNO_3 - For easier addition of solid DADN to a pressurized system, DADN was dissolved in HNO_3 so the solution could be pumped into the reactor against pressure.

Run 147: DADN dissolved in HNO_3 - crude yield, 62 percent; purity 97 percent

Run 110: Solid DADN added to reactor - crude yield, 77.7 percent; purity, 99 percent

Both runs were made without carrier. Actually, although not realized at the time, this pair of experiments confirmed Picatinny's observation that PPA and HNO_3, when prereacted, give improved yield. Because the yield of run 147 was considered to be reasonably good, it was decided to use DADN dissolved in HNO_3 as a feed in the pilot plant.

Pilot Plant

Data from all pilot plant runs are shown in Table 5. Three runs were made in the batch mode and two in the continuous mode. A flow diagram for the continuous operation is shown in Figure 11.

Batch Operation - In this operation only the first disperser was used. The carrier was placed in a dry disperser and brought to the desired temperature. The PPA and a solution of DADN in HNO_3 were fed with gear pumps into the closed system. The pressure increased slowly and reached a maximum of 20 psi in 30 min. After 1 hr the product was quenched in a drum of water. The quench temperature was kept below 40°C with the addition of ice. This is the only place in the pilot plant where NO_x vapors escaped. The carrier is separated as the bottom layer after quenching. The HMX is filtered, washed, and dried.

The batch operations provided a considerable amount of information:

A. The reaction produced a considerable amount of gas if the temperature exceeded 65°C. A decomposition exotherm can occur with

TABLE 5. PILOT PLANT NITROLYSIS OF DADN TO HMX.

Run No.	Operation mode	Reactants, (g) DADN	HNO_3	PPA	Carrier type	Reaction temperature, (°C)	Reaction time, (min)	Product weight, (g)	Product[a] (percent)	HPLC analysis HMX	SEX	DADN
P-101	Batch	631	2313	5962	CCl_4	65	50	406	63.0	10	54	37
P-102	Batch	631	2313	5160	CCl_4	60	60	586	91.0	19	45	36
P-103	Batch	1262	4626	10,515	FC-48	60	60	958	74.6	81	17	2
P-104	Continuous	3087	11,350	22,120	FC-48	60	90[b]	2004	63.6	63	31	6
						60 to 70	30[c]					
P-105	Continuous	3240	11,880	25,700	FC-48	65	60[b]	2423	73.4	92	6	1
						60	20[c]					

[a]Assume molecular weight 296

[b]Conditions in first disperser

[c]Conditions in second disperser

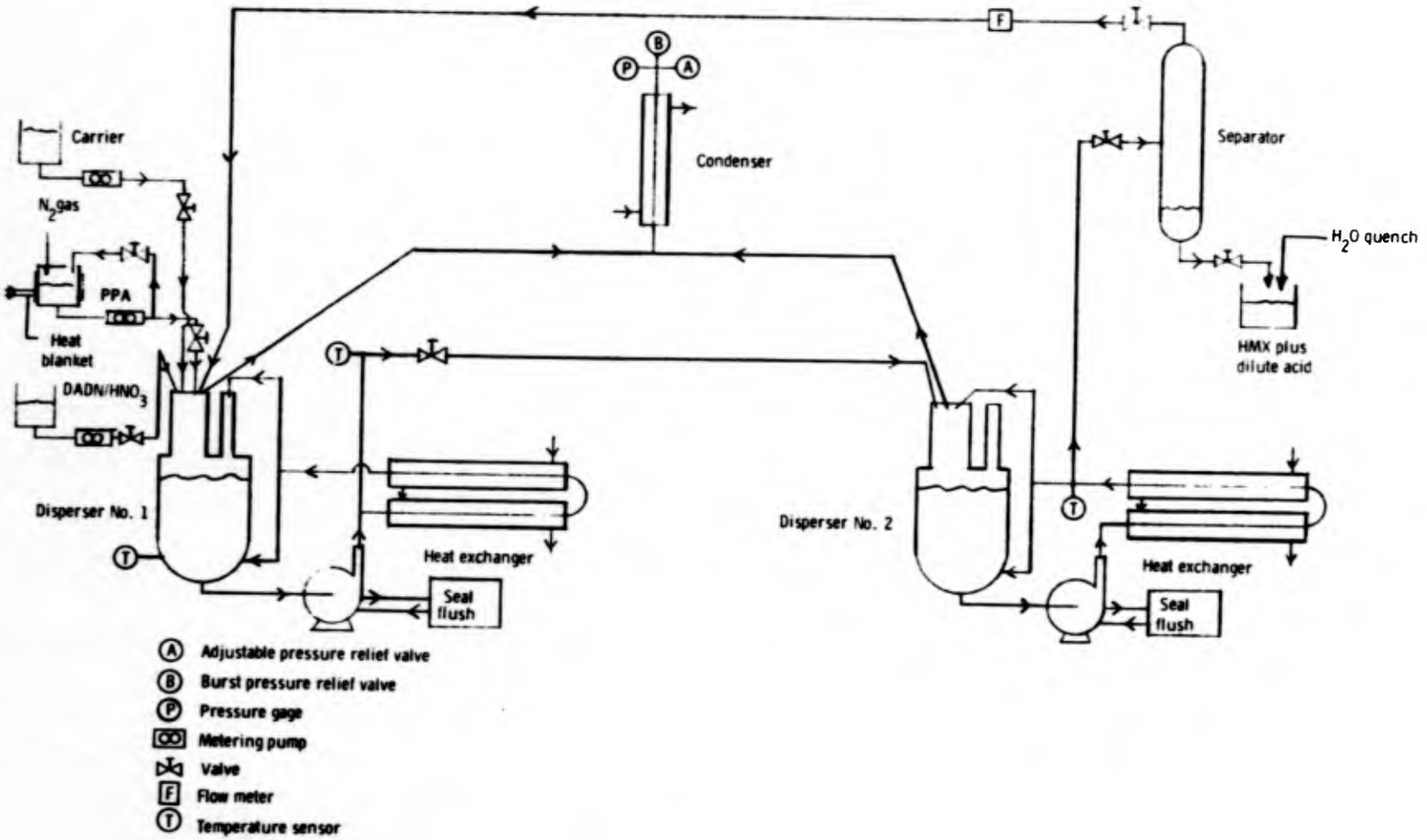

Figure 11. HMX manufacture (double disperser).

a small temperature rise which may result in a rapid pressure increase.

B. Feeding of DADN in HNO_3 gave no problems.

C. PPA was difficult to feed until it was uniformly heated to 75°C.

D. All gasket material failed except Teflon.

E. Stainless steel 304 and 316 were etched after only a few hours of exposure.

F. The total reaction media did not stick to glass with carrier present and did not attack the glass.

G. At a reaction temperature of 65°C a maximum pressure of 20 psi was reached in the system.

H. CCl_4 as carrier gave a low HMX yield.

I. FC-48 as carrier showed a reasonable HMX yield.

Continuous Operation - Two continuous pilot plant runs were made with FC-48 in the double disperser system. In run P-105 the first disperser was filled with 5 gal of FC-48. The reactants were fed the same way as in the batch operation at the following rates: (1) DADN: 30 g/min, (2) HNO_3: 110 g/min, and (3) PPA: 238 g/min.

The reaction temperature was 65°C. After 60 min, flow was started from the first disperser into the second at the same rate as the total input of reactants and carrier, a total of .2 gal/min. This was controlled by manually maintaining a constant level in the first disperser.

The reaction temperature in the second disperser was 60°C and the stay time was 20 min. Eighty min after startup, the product was continuously run from the second disperser into the quench tank. At this point the plant was in full continuous operation.

The continuous run was stopped after 108 min when all available DADN was used. The product was continuously removed from the system for another hour. After quenching, the HMX was filtered and washed with water several times before drying. This run was made without difficulties and could have

run indefinitely if more DADN had been available. Even without automation, the operation could be handled by one person.

Run P-104 was the same as run P-105 except partial overheating in the second disperser (malfunction of temperature controller on a heat exchanger) caused decomposition. Also, the feed of PPA was too low. The run was stopped to conserve the limited supply of DADN as it was obvious the decompositon observed was going to result in a lowered yield.

Analytical Studies

The HPLC analysis described in Appendix A is used in this step. HPLC scans of HMX from laboratory runs L-110 and L-122 are shown in Figures 12 and 13.

The NMRs for these runs are given in Figures 14 and 15. Very little difference between the two NMR scans can be detected. However, the HPLC chromatograms show clearly the 6-percent SEX in run 122. There is no doubt that the HPLC is the superior method.

Infrared analysis to determine the polymorph was run on each sample. Infrared analysis was also examined as a means of determining the purity of HMX. The carbonyl peak at 5.8 microns does not estblish the product composition very well. Figures 16 and 17 give the infrared spectra of runs 110 and 122.

Analytical techniques used for determinations of spent acid compositions are given in Appendix B. A description of PPA and its poly acids is included in the appendix.

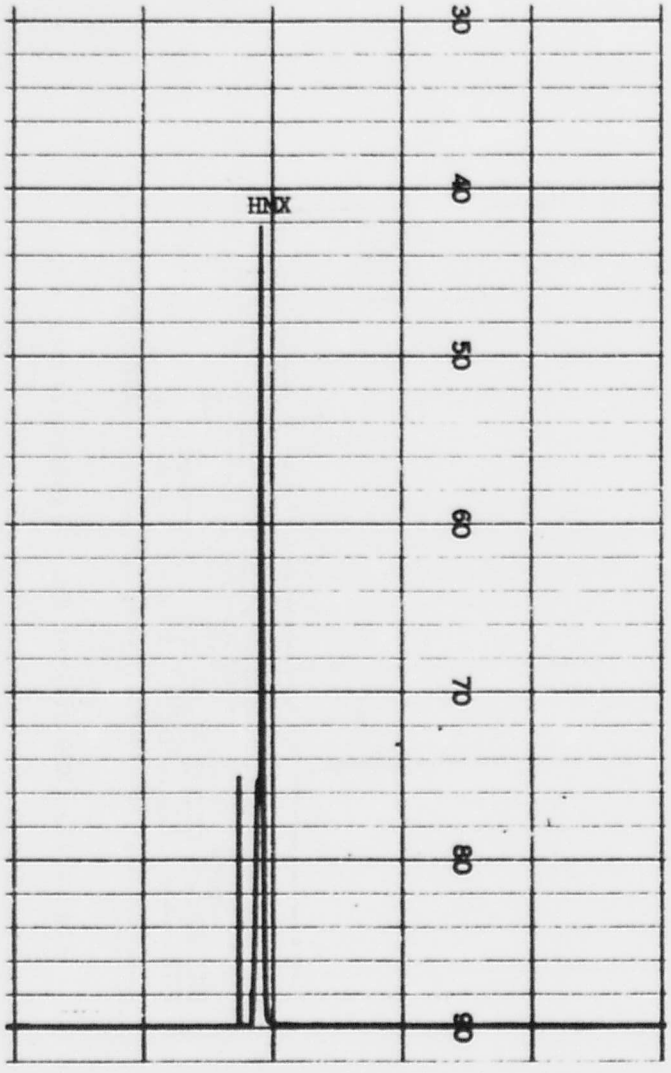

Figure 12. HPLC scan of HMX – laboratory run 110.

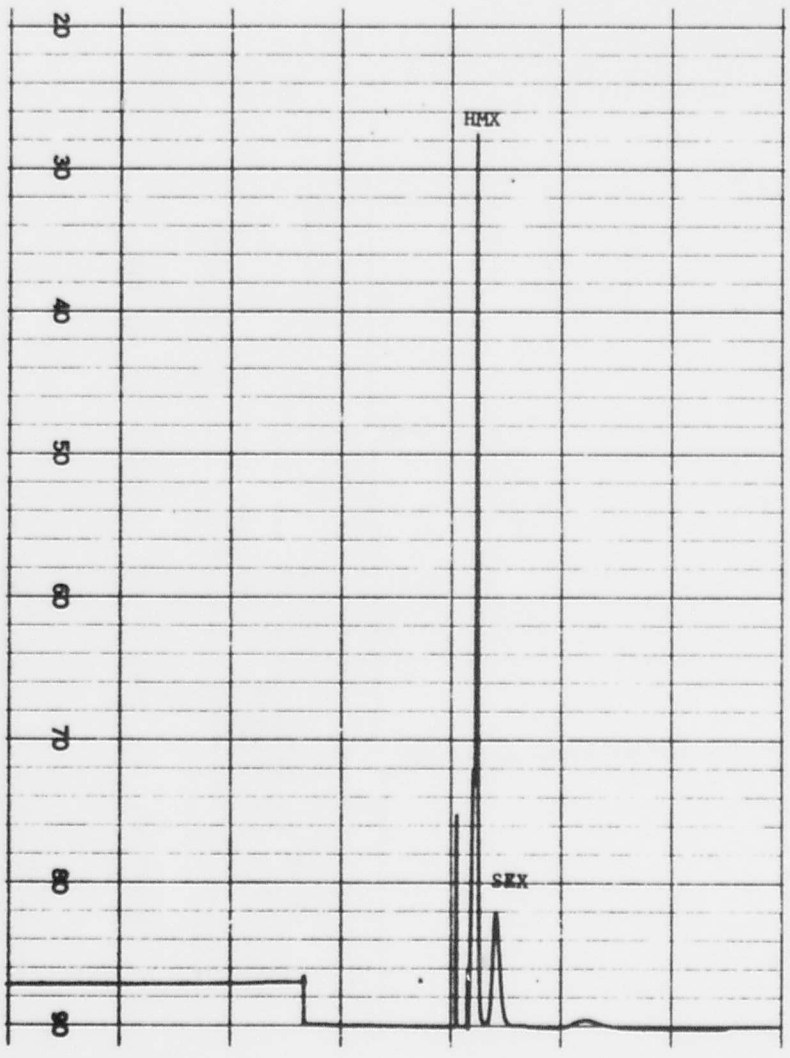

Figure 13. HPLC scan of HMX – laboratory run 122.

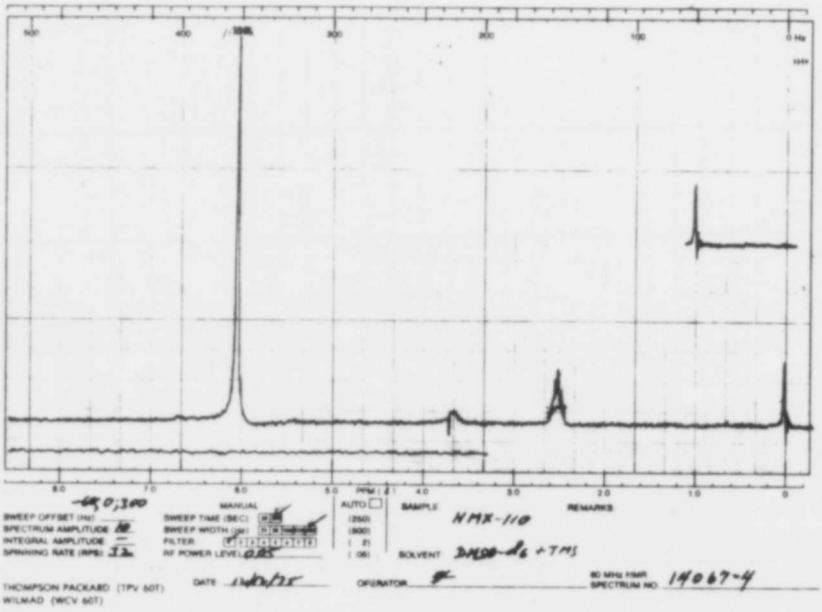

Figure 14. NMR scan of HMX – laboratory run 110.

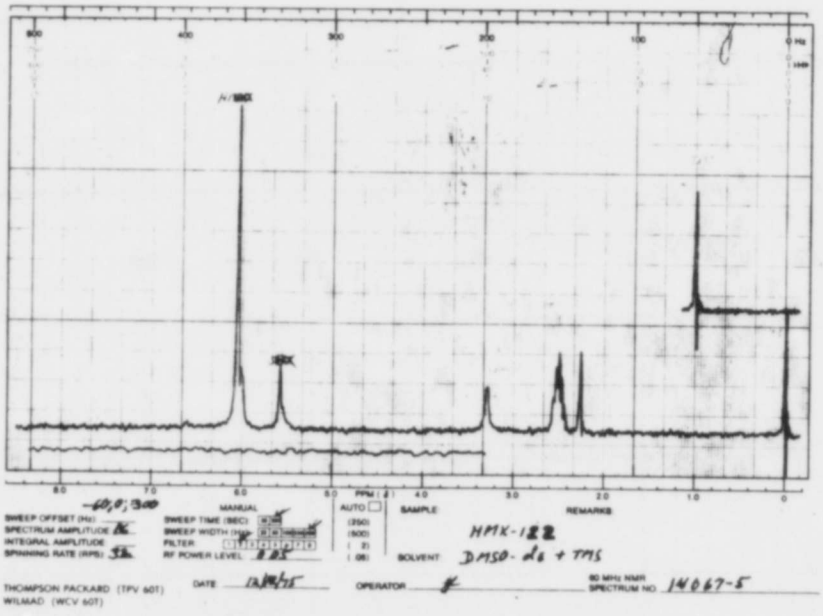

Figure 15. NMR scan of HMX – laboratory run 122.

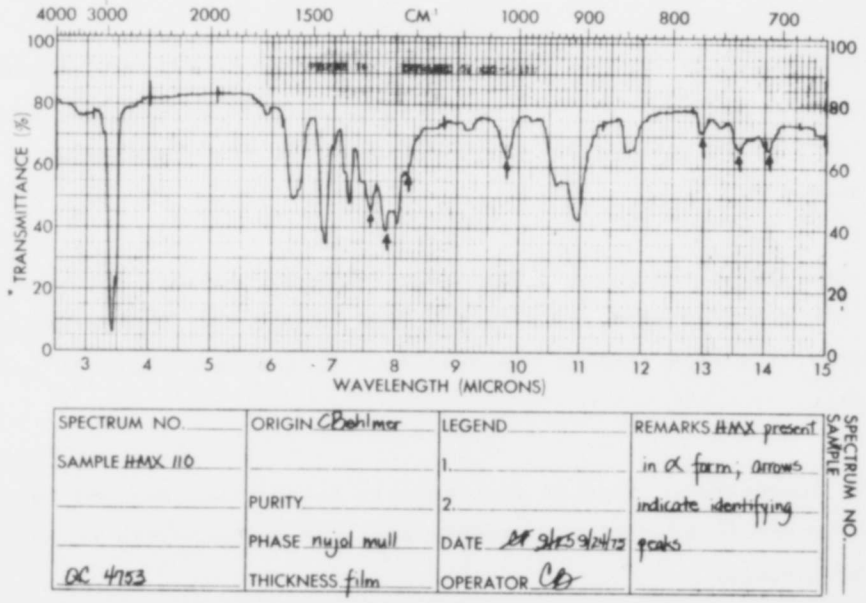

Figure 16. Infrared of HMX – run L-110.

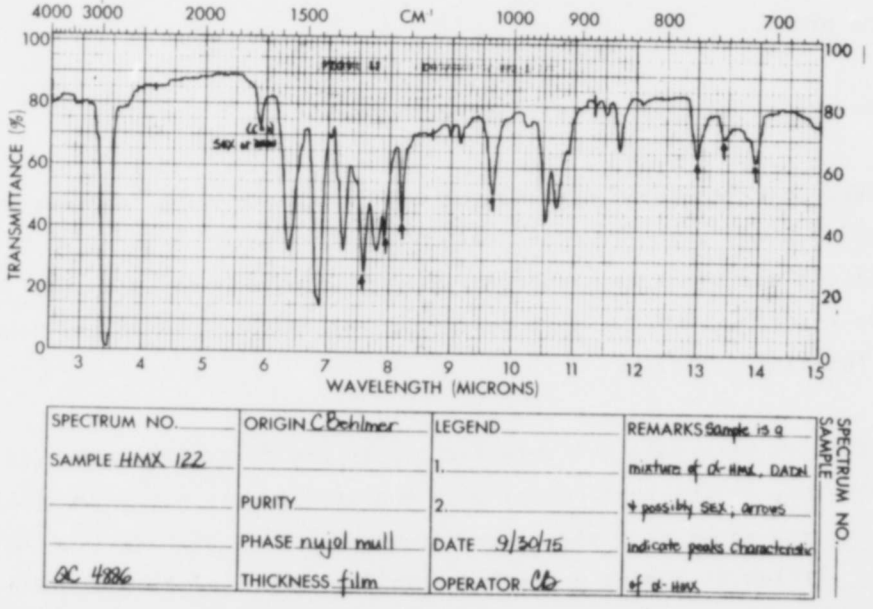

Figure 17. Infrared of HMX – run L-122

CONCLUSIONS

The new Picatinny Arsenal HMX chemistry has been successfully processed in a continuous mode in the ICP pilot plant. Processing was safe and uncomplicated. The feasibility of applying ICP to the HMX chemistry was demonstrated.

The capacity of the pilot plant scale equipment exceeds the production rates of 45 lb/hr for DAPT, 9 lb/hr for DADN, and 3.5 lb/hr for HMX by a large factor. In each step it was obvious that the rate could be increased severalfold.

It was demonstrated that it was feasible to continuously add NH_3 in the first step where it reacted with acetic acid and formaldehyde to form additional hexamine.

The dual disperser was shown to be capable of providing for complete reactions in each step with very simple equipment. The less the number of operating pieces of equipment, the less the amount of downtime in a production plant.

The ICP operates trouble-free under 20 psig.

The inert carriers used heptane for the first two steps and fluorinerts for the third step, gave clean separation from the product in all three steps. Little carrier loss occurred. Yields were comparable to equivalent laboratory results. The carriers performed well as heat sinks and as a means of reducing viscosity.

Construction materials suitable for use in the first two steps are well known. However, in the third step, with the very potent nitration media of PPA/HNO_3, it was shown that the construction materials will be limited to a few types. Teflon is a most promising candidate and performed without failure in the pilot plant. Glass showed no etching after 2 hr. All gasket materials except Teflon failed. Even the carbon insert in the pump seal had to be replaced with glass-filled Teflon.

RECOMMENDATIONS

A. Build up the ICP pilot plant to an integrated, automated system, capable of duplicating production conditions on a pilot scale.

B. Conduct studies in the pilot plant to optimize the three chemical steps and provide design parameters for the design of a pilot production line.

C. Continue Picatinny Arsenal's laboratory-scale research to improve process conditions, particularly in the third step.

D. Establish a team to quickly bring into being a pilot scale N_2O_5 generator as a possible economic alternate to the PPA/HNO_3 nitrolysis medium for the third step. Consider a combination of SRI with its research background in developing such a generator, UTRC with its expertise in developing an ozone generator, and CSD which has a considerable background in handling other oxidizers, including the somewhat similar N_2O_4.

E. Particular effort should be applied to the development of an economic means of recovering PPA from spent acid. Not much is known about this technology, and it may be the most costly step in the process.

F. A method should be developed for purifying the DAPT produced in the first step. This has a number of potential advantages. The acetic acid produced in the first step can be converted to acetic anhydride without separating it from the mixed spent acids from step II. Similarly, the spent acids from step II can be directly separated without having to remove the acetic acid from step I, and considerably less mixed acid need be used in step II. All three advantages contribute significantly to economical production of HMX, as shown in Volume III.

G. A study should be made to develop a means of returning the formaldehyde formed in step II to the beginning of the process where it will react to form more hexamine. Not only would this increase the theoretical yield from 120 to 140 percent but it would also eliminate the pollution problem which formaldehyde disposal imposes.

ABBREVIATIONS

DADN	1,5-diacetyl-3,7-dinitro-1,3,5,7-tetraazacyclooctane
DANNO	1,5-diacetyl-3-nitro-7-nitroso-1,3,5,7-tetraazacyclooctane
DAPT	diacetylpentamethylenetetranitramine
DMSO	dimethyl sulfoxide
HMX	cyclotetramethylene tetranitramine
HPLC	high pressure liquid chromatography
ICP	Inert Carrier Process
IR&D	independent research and development
LASL	Los Alamos Scientific Laboratory
NMR	nuclear magnetic resonance
OD	outside diameter
PPA	polyphosphoric acid
RDX	cyclonite (cyclotrimethylene trinitramine)
SEX	1,3,5-trintro-7-acetyl-1,3,5,7-tetraazacyclooctane
SRI	Stanford Research Institute

APPENDIX A

HMX ANALYSIS BY HPLC

Purpose

This method describes the procedure for determining the concentration of DANNO, DADN, SEX, and/or HMX in DADN, and HMX samples by high performance liquid chromatography.

Application

This method is applicable to both bench scale and pilot plant products of DADN and HMX made by the ICP in either the batch or continuous mode.

Method Summary

The sample is injected onto a packed porous column. A high pressure pump drives the sample through the column. Each sample component has a different affinity for the column packing. This different affinity causes each component of the HMX to be eluted at a different rate. The resolved components are detected by a very sensitive ultraviolet detector.

Apparatus

A. Waters Associates High Performance Liquid Chromatograph model 440/R401/M6000A equipped with an ultraviolet source detecting at 254 nmi or equivalent

B. Precision Sampling Microsyringe to 0 to 25 μl or 0 to 100 μl or equivalent

C. 1/8 in. OD by 2-in. column packed with Corasil II (Waters Associated)

Reagents

A. DANNO, 99+ percent purity

B. DADN, 99+ percent purity

C. SEX, 99+ percent purity

D. HMX, 99+ percent purity

E. Acetonitrile, ultraviolet grade-Burdick and Jackson or equivalent

F. Chloroform, ultraviolet grade-Burdick and Jackson or equivalent

Calibration

Test Conditions - Set up the instrument using the following conditions:

Ultraviolet, (aufs)	.1
Flow, (ml/min)	3.5
Chart speed, (in./hr)	12
Pump B	Acetonitrile
Pump A	Chloroform
Initial percent B	13

Preparation of Standards

A. Weigh in a 10-ml volumetric flask the following (to +.01 mg):[a]

Sample	Formula	Weight, (mg)
DANNO	$C_8H_{14}N_6O_5$	4.2 to 4.8
DADN	$C_8H_{14}N_6O_6$	7.7 to 8.3
SEX	$C_6H_{11}N_7O_7$	3.3 to 3.7
HMX	$C_4H_8N_8O_8$	1.4 to 1.6

B. Add 5 ml of acetonitrile to the flask and shake to dissolve the standards. Warm if necessary in a water bath maintained at 65°C.[b]

C. Inject 15 µl of the standard solution.

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[a] If DADN samples are to be analyzed only DANNO and DADN need be weighed.

[b] Do not heat sample above 65°C or decomposition of the sample will occur. Cool the sample to room temperature. Dilute to the mark with Acetonitrile.

Calculations

Determination of Molar Concentration - Determine the concentration of each component in moles/liter using the following formula:

$$\text{Concentration, moles} = \frac{\text{g, component in 1000 ml}}{\text{molecular weight component}}$$

$$= \frac{(\text{g, component in 10 ml})\ (100)}{(\text{molecular weight component})}$$

$$= \frac{X}{(Y)\ (10)}$$

where X = component weight, mg

Y = component molecular weight, g/mole

DANNO = 274 g/mole

DADN = 290 g/mole

SEX = 293 g/mole

HMX = 296 g/mole

Determination of Molar Response Factor, E

A. The absorption of light is governed by Beer's Law:

$$A = Ebc$$

$$E = \frac{A}{bc}$$

Where A = Absorption, absorbance units

b = cell path length, 1 cm

c = component concentration, moles/liter

E = molar response factor, $\frac{\text{liters}}{\text{cm-mole}}$

B. Measure the absorption of the HMX peak to ±.0001 absorbance unit (au).

C. Determine the E value for HMX using the equation as in step A.

D. Repeat steps B and C for DANNO, DADN, and SEX.

Procedure

A. Weigh 7 to 8 mg (to ±.01 mg) of sample into a 10 ml volumetric. Add about 5 ml of acetonitrile to the flask and shake to dissolve the sample, warming if necessary in a 65°C water bath. Cool to room temperature. Dilute to the mark with acetonitrile.

B. Inject 15 µl using the same chromatographic conditions as in the Test Conditions section.

Calculations

Peak Area

A. Draw a baseline for the HMX peak.

B. Measure the peak height to the nearest .1 mm.

C. Mark the peak at a distance equaling one half the peak height. At this distance measure the peak width to the nearest .1 mm.

D. Calculate the peak area, D:

D = peak area
= height X width at half height

E. Obtain the corrected peak area, F:

F = corrected peak area
+ (D) (E)

F. Repeat steps for DANNO, DADN, and SEX.

Normalization

A. Total the corrected peak areas referred to as F. This total is called G.

B. To obtain the percent concentration of a particular component, use the following formula:

$$\text{weight-percent} = \frac{(F)(100)}{G}$$

APPENDIX B

ACID ANALYSIS FOR HMX MANUFACTURE BY THE NEW CHEMISTRY

INTRODUCTION

In applying the new chemistry to the manufacture of HMX, it is necessary to use concentrated sulfuric, nitric, and polyphosphoric acids. These acids must be analyzed for concentration and purity when received and before use. Mixtures of these acids as premixed feed and from in-progress reactions must also be known. Finally, the analysis of these acids in waste streams is needed to evaluate their economic recovery.

A great deal of research has been done to develop analytical methods for the assay of these mixed acids. This appendix relates progress that has been made in the area of acid analysis and discusses the methods encountered, the accuracy expected, and an understanding of the analytical process.

Nitric Acid

The determination of 90 to 100-percent pure nitric acid[a] is relatively straightforward. A weighed sample of acid is titrated with standardized sodium hydroxide to a pink phenolphthalein end point. Concentrated nitric acid fumes readily so it must be weighed by difference in a Lunge Pipet. The sample should be added to a titration vessel containing water so that losses by evaporation are minimized. Precision of the analysis is $\pm$.04 percent.

Sulfuric Acid

The determination of 90 to 100-percent pure sulfuric acid[b] is similar to that for nitric acid. However, the sample must be weighed by

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[a]CSD Method IQCL-1017, Test Method for Nitric Acid (95 to 100 percent).
[b]CSD Method IQCL-1022, Analysis of H_2SO_4 (90 to 100 percent).

difference as it is highly hydroscopic. Precision of the analysis is ±.04 percent.

Nitric-Sulfuric Acid Mixtures

Nitric-sulfuric acid[a] mixtures are used in the nitration of DAPT to DADN. The acid mixture is titrated with a standardized base to determine the total acidity. A sample evaporated 2-1/2 hr on a steam bath leaves a residue of sulfuric acid which is titrated with a standardized base. The difference in acidities between samples is the nitric acid value. The water may be found by difference or by a Karl Fischer titration. The precision for these analyses is about ±.08 percent for nitric acid, ±.04 percent for sulfuric and ±.1 percent for water.

The sulfuric acid has also been determined as sulfate by precipitation with barium and as nitrate colorimetrically. These analyses are time consuming and precision is ±.4 percent as sulfate and ±2 percent as nitrate.

POLYPHOSPHORIC ACID (PPA)

The PPA[b,c] used in nitration of DADN to HMX is supplied by FMC. FMC describes this acid as an equilibrium mixture of orthophosphoric, pyrophosphoric, and higher polyphosphoric acids with the general formula as $H_{(n+2)}P_nO_{(3n+1)}$.

The analysis of PPA is complicated because each of the condensed acid species in the PPA has a difference acidity. An early attempt to analyze PPA by Bell[d], used wet chemical methods. However, his technique resolved

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[a]CSD Method IQCL-0013, Test Method for Nitric Acid, Sulfuric Acid, and Water in Spent Nitrating Acid

[b]Spoog and West, Fundamentals of Analytical Chemistry, 2nd Ed., Holt, Richard and Winston, Inc., N.Y., 1969.

[c]Van Wazer, Phosphorous and Its Compounds, Volume I, Interscience Publishers, Inc., New York, 1958.

[d]Bell, Ind. Eng. Chem., 40, 1464, 1948.

only short chain acids up to tripolyphosphoric acid (n=3). It was not until the advent of paper chromatography that the higher components of PPA were resolved quantitatively. Huhti and Gartaganis, using ascending paper chromatography and a nonaqueous solvent, separated the components of PPA up to the nonphosphoric acid (n=9).[a]

The best present method of PPA species identification is by ion-exchange chromatography. Jameson, using this technique,[b] resolved and quantitatively analyzed condensed acids species up to n=15. His study on many PPA samples showed that the percent composition of the condensed acids depended only upon the total P_2O_5 concentration of the sample. A graph of Jameson's is reproduced in Figure B-1. The precision on analysis of the total acid is ±.2 percent while that for individual species is ±2 percent.

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[a] Huhti and Gartaganis, Con. J. Chem. 34, 785, 1956.

[b] Jameson, J., Chem. Soc., 752, 1959.

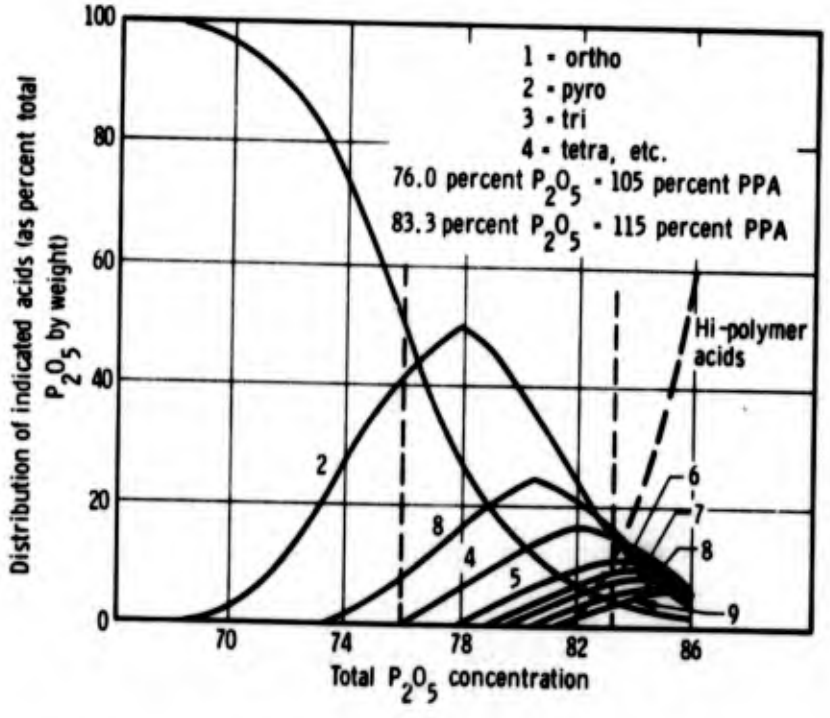

Figure B-1. Composition of concentrated phosphoric acids.

Since assembling equipment for this analysis is both time-consuming and costly alternative methods for analyzing PPA were investigated. One method was a potentiometric titration of PPA. The results of this titration were two inflection points which were not steep enough to obtain good-equivalence points.

Another technique tried was a nonaqueous titration in formamide and in dimethyl-formamide. Neither of these solvents gave satisfactory equivalence points.

Since the PPA composition is proportional to the P_2O_5, analysis of a sample for its P_2O_5[a] content provides the necessary information. This is easily done by hydrolyzing PPA in an excess of boiling water and titrating to its equivalence points with a standardized base. The precision is $\pm$.4 percent.

Phosphoric Acid - Acid Mixtures

The analysis of mixtures containing two weak acids is more difficult than a strong acid-weak mixture. The acidity titration curve for a mixture of phosphoric acid and acetic acid is not additive, as is the case with a strong and weak acid mixture, due to the buffering effect of the phosphate and acetate ions. The phosphoric acetic titration curve shows three inflection points which can be resolved. The first peak is the first proton of phosphoric acid, the second is acetic acid, and the third identifies the second proton of phosphoric acid. Analysis of synthetic acid mixtures showed that good equivalence points are obtained for the phosphoric and acetic acids. Results, as determined by subtraction, are accurate to $\pm$.5 percent.

The determination of phosphate may be done calorimetrically,[b] but it is less accurate than titration because of sample dilution. A gravimetric method also exists, but this has not been investigated.

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[a] CSD Method IQCL-0990, Test Method for Polyphosphoric, Superphosphoric Acids (P_2O_5) Analysis.

[b] CSD Method IQCL-4021, Determination of Orthophosphates - Colorimetric.

Phosphoric - Acetic - Nitric Acid Mixtures

The introduction of nitric acid to the mixture presents no new major problems. However, the first peak in the titration curve is the nitric and phosphoric acids. The third component means that compositions are not calculated directly. However, the nitric and acetic acids can be evaporated on a steam bath, then the remaining phosphoric acid titrated. The nitric acidity is obtained by subtraction. The percent compositions are calculated with a precision of ±.5 percent.

A sample of spent acid from bench scale run 147 was analyzed with the following results:

Bench scale run 147 component	Quenched acid analysis (composition, (percent)
H_3PO_4	43.36
HNO_3	7.26
CH_3COOH	1.03
H_2O	45.4
Organics	Residual

Sulfuric - Nitric - Acetic Acid Mixtures

Mixtures of strong and weak acids are analyzed similarly to mixtures of weak acids. Titration curves for strong and weak acid mixtures show two equivalence points, the first being the strong acid. In the case of sulfuric-nitric-acetic mixtures the sulfuric and nitric acid will be titrated first. The sulfuric mixture can be obtained from an evaporated sample titrated with a standardized base. Concentrations for nitric acid and acetic acid are calculated by subtraction of the sulfuric acid concentration from the titration curve. The precision obtained from synthetic mixtures was ±.5 percent for each acid component. The results from a spent acid[a] sample after quench on DAPT-DADN pilot plant run 10 are shown below:

[a]CSD Method IQCL-0010, Waste Acid Analysis from DADN Nitration.

Plant run 10 component	Quenched acid analysis composition, (percent)
H_2SO_4	22.29
HNO_3	1.41
CH_3COOH	2.38
H_2O (Karl Fischer)	74.55
Total	100.63

CONCLUSION

The methods of analysis discussed in this paper have been successfully used to determine the compositions of many pure and mixed acid samples. Synthetic acid mixtures with many combinations of acids have been formulated and analyzed with good results. Spent acids from the DAPT to DADN nitration and from the DADN to HMX nitrolysis were analyzed for use in the economic evaluation (Volume III).