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ALTERNATIVE PROCESSES FOR HMX MANUFACTURE

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Three new procedures were developed for preparing HMX from hexamine, one involving TAT as the intermediate; the others, DADN and DANNO. The DADN process was studied in some detail; the other two were not developed beyond the exploratory stage. Overall yield (hexamine to HMX) in the DADN process is about 13% higher than that of the conventional Bachmann process, and the acetic

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20. ABSTRACT (Continued)

anhydride requirement is considerably lower. The first two steps were demonstrated in continuous pilot plant operation, yielding about 14 lb/hour of DADN in simple equipment. Application of the inert carrier concept (ICP) did not show promise. A cost study indicated that the DADN process offered no advantage over the Bachmann, mainly because two additional acids (sulfuric and polyphosphoric) are used.

TABLE OF CONTENTS

TABLES

FIGURES

INTRODUCTION

As principal manufacturer of explosives for all DOD applications, the U.S. Army is responsible for a major industrial complex which must be retained in a viable state at all times to meet the needs of national emergencies. The realization that the existing industrial capacity, now 30 years old, may not stand another cycle of deactivation and wartime reactivation has, therefore, required the planning of a multi-billion dollar plant modernization program. At the same time, a changing economic and political climate has drawn increased attention to the cost effectiveness of explosives, to the massive pollution problem associated with explosives manufacturing, and to the vulnerability of the sole installation that manufactures our more powerful explosives, RDX and HMX.

The Army's explosive research program is, therefore, placing heavy emphasis on the search for new synthetic routes which may lead to cheaper, cleaner, continuous processes, and provide flexibility in meeting emergency requirements on a geographically dispersed basis. The work reported here represents one facet of the program as it relates to HMX synthesis; it is particularly important because, after 20 years of fruitless investigation in university and military laboratories, the field was suspected to be barren of opportunity.

HMX, 1,3,5,7-tetranitrotetrazocine, is the most powerful military explosive, but widespread application is limited by its high cost and availability. Although HMX was first discovered in 1941 (ref. 1,2), the nitrolysis of hexamethylenetetramine by the Bachmann process, as described by Castorina and coworkers (ref. 3), is still the only manufacturing process. The process (fig. 1) has undesirable features, including a poor yield on a methylene basis, a high usage of acetic anhydride, and a slow rate of production.

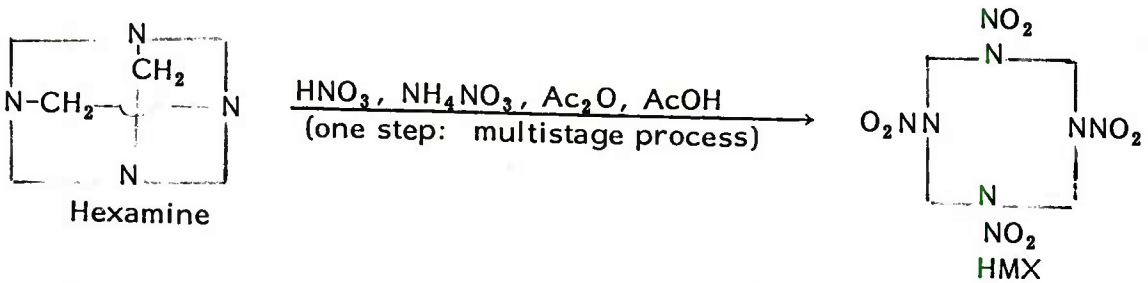


Figure 1. Present HMX process.

Numerous investigators recognized the difficulties with the existing process and alternative synthetic routes were sought, including the cyclization reactions involving linear molecules, such as the nitramines, and formaldehyde (ref. 4,5,6,7), the nitrolysis of fused ring heterocycles containing the eight-membered tetrazocine ring (ref. 4,5,6,7), and the nitrolysis of hexamine isosteres (ref. 8,9,10). All of these efforts resulted in poor yields of HMX or none at all. Other investigations were directed to the improvement of the existing process by variation of the process parameters (ref. 4,11,12). These studies, although indicating significant improvement, have not as yet resulted in major cost reduction.

During the period 1971 to 1975 the Energetic Materials Division of ARRADCOM initiated and conducted a program toward the development of alternative processes for HMX manufacture. Three processes were studied. These processes, the "TAT PROCESS," the "DANNO PROCESS," and the "DADN PROCESS," are described and discussed in this report. The exploratory development phase for each process is discussed separately for purposes of clarity. This work was conducted mainly in-house, with substantial support from the University of Idaho. The advanced laboratory and pilot studies of the most promising process, the DADN PROCESS, conducted jointly by this laboratory, Los Alamos Scientific Laboratory, and United Technologies' Chemical Systems Division, are presented. Finally, a comparison of the DADN process and the existing HMX process is given.

EXPLORATORY DEVELOPMENT

TAT Process

The TAT approach to HMX, as conducted in the laboratory, is a multistep procedure which uses the same raw materials as the existing process, but relies on quite different chemistry.

The overall schematic sequence used in this method of preparing HMX is depicted in figure 2. Starting from either hexamine or formaldehyde and ammonia, the synthesis proceeds via reaction with acetic anhydride through two intermediate compounds, DAPT and TAT; the latter finally undergoes nitrolysis to HMX.

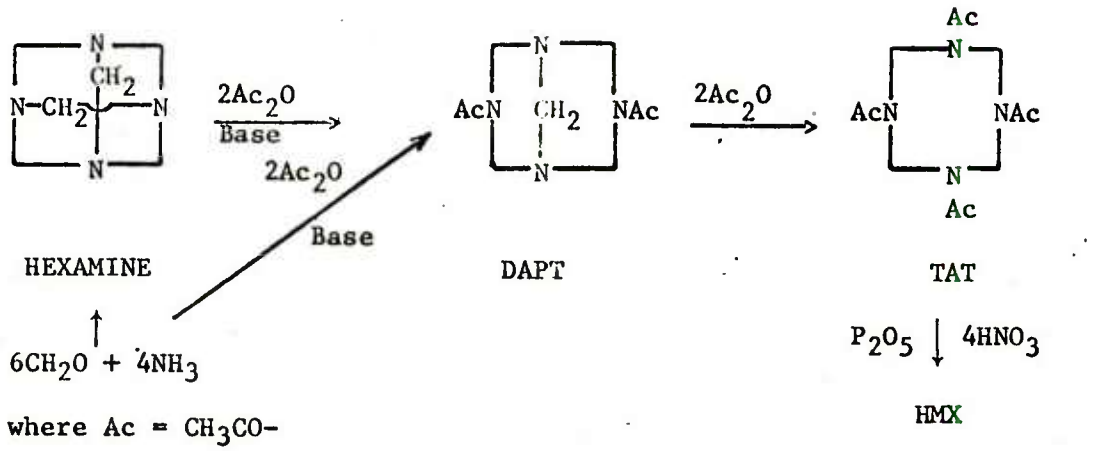


Figure 2. The TAT process.

TAT is a heterocyclic compound based on an eight-membered ring. It has a six-membered analogue, TRAT (triacetylhexahydrotriazine), which can be nitrolyzed to RDX (ref. 13), the six-membered analogue of HMX, and is a reaction intermediate in a new RDX synthesis previously investigated (refs. 6, 14). TRAT can also be prepared by the acetolysis of hexamine (ref. 15), which indicates the flexibility of the new approach. The three-step procedure is described below.

DAPT Synthesis

DAPT (1,5-diacetyl-3,7-endomethylene-1,3,5,7-tetrazacyclooctane) (fig. 2) has been prepared from hexamine and acetic anhydride by several previous investigators, but always in poor yields and under anhydrous conditions. Dominikiewicz (ref. 16) obtained a 30% yield in anhydrous ether; G. C. Bassler (ref. 17) reported 10 to 19% yields in chloroform. In 1949 a study was made by Aristoff and co-workers (ref. 18), who obtained a 6.5% yield without solvent and made repeated unsuccessful attempts to improve the yield. Recently, Hodge (ref. 19) reinvestigated the preparation of DAPT and reported yields varying from 9 to 45%.

At the start of our effort to find alternative routes to HMX, realizing that DAPT could be a key intermediate, we repeated the above experiments with essentially the same results. During the course of these experiments we made two important observations. The first was the course that the anhydrous acetylation took as a function of temperature. At temperatures from 0°C to ambient, we noted that yields of DAPT in the order of 6 to 30% were obtained. As the temperature was elevated,

the yields of DAPT decreased and TRAT became the major product (ref. 15). The second observation was even more significant. We noted that the presence of water could be tolerated in the reaction system, and its presence enhanced the yields of DAPT. A series of hexamine acetylations was, therefore, run under aqueous conditions (table 1). This series of reactions showed that DAPT could be obtained in yields, of 65 to 68% by reaction of hexamine (0.1 mole) with acetic anhydride (0.25-0.3 mole) in 50 ml of water at temperatures from -10° to 10°C. Incorporation of 0.25 to 0.6 molar quantities of basic additives such as $NaHCO_3$ or $KHCO_3$, Na_2CO_3, or K_2CO_3, or NaOH, increased the DAPT yield to approximately 80%. One additive, ammonium acetate, produced a rather startling yield increase: at the 0.25 molar level, the DAPT yield rose to 86%. At lower levels, the yield improved even further. The optimum molar quantity of ammonium acetate was found to correspond to a slight excess over that required to convert the liberated formaldehyde back to hexamine for further reaction with acetic anhydride.

Although the yield of pure isolated DAPT, using 0.3 mole of acetic anhydride and 0.081 mole of ammonium acetate, was found to be 100% based on hexamine, the actual yield was determined to be approximately 115% by nmr analysis. The additional 15% of theoretical based on the initial amount of hexamine is due to the resynthesis of hexamine from the formaldehyde librated during the reaction and ammonium acetate. This point will be discussed further under Advanced Development.

In an effort to reduce the volume of reactants, the effect of water on DAPT yield was studied both with and without ammonium acetate. The results are depicted in figure 3. Based upon this work, it is clear that the mole ratio of water to hexamine can be reduced from the initial 28:1 (50 ml H_2O) to 3.9:1 (7 ml H_2O) without affecting the yield of isolated DAPT.

This exploratory effort led to the following procedure for the preparation of DAPT (refs. 20, 21):

> "Fourteen grams of hexamine (0.1 mole) and 6.2 grams of ammonium acetate (0.081 mole) were added to 7 ml of water which was contained in a 50 ml flask held at 5-10°C. 30.6 grams (0.3 mole) of acetic anhydride was then added to this slurry over a period of 60 minutes while stirring and maintaining the temperature between 5 and 10°C. The resulting clear viscous solution

Table 1. DAPT preparation via hexamine acetolysis[a]

Ac_2O mole	Base added: Type[b]	Base added: Mole	Temp (°C)	Ac_2O addition (min)	Age (min)	DAPT: Crude (g)	DAPT: Melting point (°C)	DAPT: Pure[c] yield %
0.25	None	None	-10	45	30	14.4	192	68
0.25	None	None	10	60	30	13.8	192	65
0.6	NaOH	0.6	10	60	60	16.5	192	78
0.2	NaOH	0.2	0	70	120	3.18	192	15
0.4	NaOH	0.4	0	115	60	9.12	192	43
0.4	NaOH	0.4	-15	60	60	15.9	192	75
0.4	NaOH	0.4	-15	130	120	16.3	192	77
0.6	NaOH	0.6	-15	60	60	17.2	192	81
0.6	Na_2CO_3	0.3	10	60	60	17.0	192	80
0.6	$NaHCO_3$	0.6	10	60	60	16.75	192	79
0.6	K_2CO_3	0.3	10	60	60	16.75	192	79
0.6	$KHCO_3$	0.6	10	60	60	16.1	192	77
0.35	Na acetate	0.25	-10	60	30	16.2	192	76
0.3	Na acetate	0.25	+10	45	40	15.1	192	71
0.3	Na acetate	0.25	-10	60	40	15.8	192	75
0.25	Na acetate	0.50	-10	50	40	15.2	192	72
0.6	NH_4 acetate	0.25	-10	60	30	14.9	192	70.5
0.25	NH_4 acetate	0.25	+5	50	30	17.78	192	84
0.25	NH_4 acetate	0.25	10	60	30	20.2	192	96
0.25	NH_4 acetate	0.25	5	60	35	18.2	192	86
0.25	NH_4 acetate	0.25	-10	40	30	17.3	192	81.5
0.2	NH_4 acetate	0.25	-10	45	30	13.6	192	64
0.3	NH_4 acetate	0.067	10	30	60	20.0	192	94
0.3	NH_4 acetate	0.081	10	60	30	21.2	192	100

[a] In all reactions, 0.1 mole of hexamine was used.

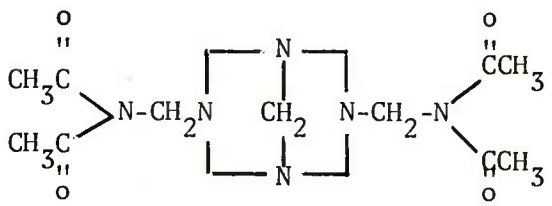
[b] In reactions using sodium or ammonium acetate, 50 ml of water was used as the solvent medium; for other bases, 50 ml of water was used to dissolve the hexamine and this solution was added to 120 ml of 20% aqueous base prior to anhydride addition.

[c] Yield based on initial hexamine used.

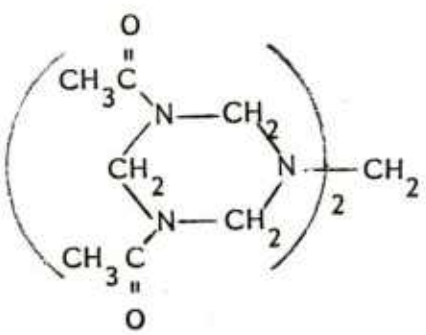
was then aged for 30 minutes and finally evaporated under vacuum on the steam bath. After recrystallizing the solid mass, obtained in this manner, from boiling acetone, 21.2 grams of DAPT melting at 192°C was isolated. The yield was 100% based on the initial quantity of hexamine used."

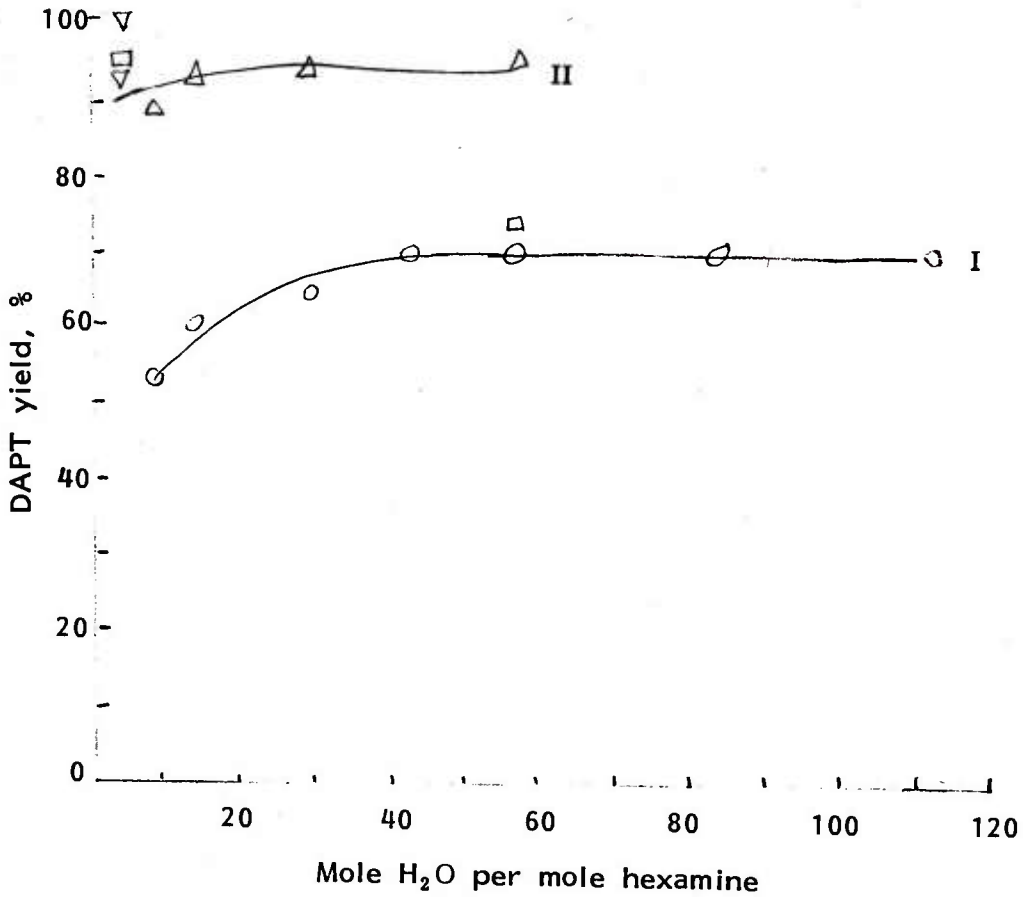
Further efforts to refine the reaction are reported under Advanced Development.

It should be pointed out that, at the end of recrystallization and evaporation of the remaining acetone, a viscous oil is obtained. We have isolated a very small amount of solid melting at 222°C from this oil. The material has been characterized and the proposed structure is in accord with the analytical data, nmr spectra, and mass spectral pattern. We have proposed that this material has the following structure (ref. 21):



The formation of a compound also melting at 222°C was likewise noted many years ago (ref. 22) to result from the reaction of acetic anhydride and hexamine. On the basis only of analysis for C and H and aqueous hydrolysis to N,N' methylenebisacetamide, the compound was concluded to be N,N'-methylenebisdiacetamide. The latter material was not prepared at that time for comparison with the compound melting at 222°C and was, in fact, unknown until later (ref. 23). We have prepared it, verified the reported melting point (96°C), and noted that it differs in other respects from our proposed structure. A different structure than that proposed by us has been suggested by Farminer (ref. 24). This structure:





I. Hexamine + Ac_2O + H_2O

II. Hexamine + Ac_2O + $NH_4OC(=O)CH_3$

I
- ○ = 2.5 mole Ac_2O
- □ = 3.0 mole Ac_2O

II
- △ = 2.5 mole Ac_2O + 0.67 NH_4Ac
- □ = 3.0 mole Ac_2O + 0.67 NH_4Ac
- = 3.0 mole Ac_2O + 0.81 NH_4Ac

Figure 3. DAPT yield vs molar ratio water: hexamine.

has the same empirical formula and molecular weight; we have not determined which of these structures is correct.

This aqueous acetolysis reaction appears to be general for the formation of acyltetraazabicyclo (3.3.1) nonanes. In addition to DAPT, the following derivatives were prepared (ref. 21). The corresponding yields and melting points are also given.

> 3,7-Diformyl-1,3,5,7-tetraazabicyclo (3.3.1) nonane (22%; 251°C), 3,7-Dipropionyl-1,3,5,7-tetraazabicyclo (3.3.1) nonane (52%; 132°C), 3,7-Di-n-butyryl-1,3,5,7-tetraazabicyclo (3.3.1) nonane (52%; 87°C), and 3.7-Dibenzoyl-1,3,5,7-tetrazabicyclo (3.3.1) nonane (13%; 181°C).

Using the same procedure, Thyagarajan (ref. 15) recently reported that the 3,7-di-(trichloroacetyl) analogue could be prepared in 5% yield.

Two other methods for DAPT preparation were developed under this program. As shown in figure 2, DAPT can be prepared from formaldehyde and ammonia in aqueous solution by acetolysis in the presence of base. The yield thus far attained by this method has only been 82% (table 2), but it is believed that further work will improve this to the level found for the acetolysis of hexamine. This is a reasonable assumption, as the acetolysis of a mixture of CH_2O and NH_3 proceeds via hexamine, in situ. The major advantage of the formaldehyde-ammonia procedure is that the isolation of hexamine, required in the existing HMX process, would no longer be necessary and, in addition to the added flexibility, process costs would be reduced.

The other method developed uses a variation of the hexamine-anhydride system already described, that is, the substitution of ketene for acetic anhydride (refs. 21, 26). Yields of pure DAPT, as shown in table 3, were found to be as high at 65% based on hexamine; however, no attempt was made to optimize this method. This procedure also employed water as the medium, since it is known that ketene reacts sufficiently slowly with water to permit its use as a reaction solvent in the acetylation of amines (ref. 27).

A comparison of ketene vs acetic anhydride economics indicated that the use of ketene could save 0.5 cent per lb of anhydride used if equivalent on a water removal basis. Further study of the ketene-DAPT synthesis may be warranted on the basis of this observation.

Table 2. DAPT from formaldehyde and ammonia

CH_2O[a] (mole)	NH_3[b] (mole)	1st stage[e] Addition time (min) / Addition temp (°C)	Age time (min) / Age temp (°C)	NaOAc[c] anhyd (mole)	Water[d] (ml)	2nd stage[e] Ac_2O (mole)	Addition time (min) / Addition temp (°C)	Age time (min) / Age temp (°C)	DAPT yield (%)	MP (°C)
0.6	0.4	20 / 15-20	10 / 15-20	0.42	50	0.42	60 / 5-10	15 / 10	50	192
0.6	0.44	20 / 15-20	10 / 15-20	0.42		0.42	60 / 5-10	15 / 10	62	192
0.6	0.44	20 / 40	15 / 40	0.42		0.42	60 / 5-10	15 / 10	71	192
0.6	0.44	20 / 40	60 / 40	0.42		0.42	60 / 5-10	15 / 10	76	192
0.6	0.48	20 / 40	15 / 40	0.42		0.42	60 / 5-10	15 / 10	73.4	192
0.6	0.44	20 / 40	15 / 40	0.3		0.3	60 / 10	15 / 10	64	192
0.66	0.4	20 / 40	15 / 40	0.42		0.42	60 / 10	15 / 10	61	192
0.6	0.48	20 / 40	15 / 40	0.42		0.42	60 / 10	15 / 10	78	192
0.6	0.48	20 / 40	15 / 40	0		0.42	60 / 10	15 / 10	70.5	192
0.6	0.48	20 / 40	15 / 60	0.42		0.42	60 / 10	15 / 10	82	192

[a] 37% aqueous CH_2O used.

[b] 28% NH_4OH used.

[c] Added as 3 hydrate at 5-10°.

[d] Water added at 5-10°.

[e] Mode of addition, NH_4OH to CH_2O, then NaOAc, water, and finally Ac_2O.

Table 3. DAPT from hexamine-ketene

Hexamine (mole)	Ketene[a,b] (mole	Ac_2O[c] (mole)	Additive	Additive (mole)	Temp (°C)	Addition time (min)	Aging time (min)	DAPT (g)	MP (°C)	DAPT yield (%)
0.1	0.94	--	CH_3COONa	0.25	20	120	120	13.0	188-90	65
0.1	0.94	--	CH_3COONa	0.25	10	120	90	11.5	188-90	54
0.1	0.94	--	CH_3COONH_4	0.25	15	120	90	11.5	188-90	54
0.1	0.94	--	--	--	5	120	90	10.6	185-90	50
0.1	0.94	--	--	--	20	120	60	12.4	187-90	58
0.1	0.94	--	--	--	30[d,e]	120	60	9.3	187-90	44
0.1	0.47	--	--	--	5	60	60	8.5	184-90	40
0.1	1.41	--	--	--	20[f,g]	180	60	8.4	187-90	39
0.1	--	0.25	--	--	10	60	30	13.8	192	65
0.1	--	0.25	--	--	-10	60	30	14.4	192	68

[a] Rate of ketene addition was 0.47 mole/hr.

[b] 175 ml of water used as solvent.

[c] 50 ml of water used as solvent.

[d] 2.95 g of TRAT also isolated; mp 68-71.

[e] Oil remaining after DAPT isolation contained TAT, TRAT, DAPT, and hexamine.

[f] 2.90 g of TRAT also isolated.

[g] Oil remaining after DAPT isolation; see note e.

TAT Synthesis

TAT (1,3,5,7-tetraacetyl-1,3,5,7-tetrazacyclooctane) (fig. 2) is, like DAPT, also a known compound, but its preparation in 20 to 35% yields was cited only in unpublished government reports (ref. 17). The preparation described consisted of refluxing DAPT in acetic anhydride containing a trace of acetyl chloride.

In the present investigation, we have duplicated the referenced reaction and found that TAT yields of 48% were obtainable. It has also been determined that TAT can be prepared from DAPT and Ac_2O, without acetyl chloride, in yields as high as 70% by the following method:

$$\text{DAPT} + 6\ Ac_2O \xrightarrow{110°C} \text{TAT}$$

The data compiled using this high temperature anhydrous acetylation are shown in table 4.

Improved yields have been realized in reactions involving the following scheme (ref. 28):

$$\text{DAPT} : 2\text{AcCl} : 6Ac_2O : 4\text{NaAc} \xrightarrow[10°C]{\text{AcOH}} \text{TAT}$$

We have found that yields of 75 - 90% of TAT can be obtained under the proper conditions. The experimental data are summarized in table 5. A mixture of acetic anhydride and acetyl chloride is required, since poor yields resulted when using either alone (runs 13-15). Either acetic acid or chloroform can be used as reaction solvents, and water can be present or the reaction can be run anhydrous (run 13). In all cases, we employed a reaction temperature below 20°C, and added sodium acetate. The order of addition can be varied, except that the acetyl chloride must be added after the sodium acetate (runs 6,9,10,11).

The results indicate that acetyl chloride takes part in the scission of the endo-methylene bridge in DAPT (fig. 4). An unstable intermediate, presumably chloromethyltriacetyltetrazacyclooctane (I), is formed which,in turn,reacts with sodium acetate to form the acetoxymethyltriacetyl derivative (II); this on acetolysis with Ac_2O is

Table 4. Synthesis of TAT: high temperature method

DAPT g (mole)	Ac_2O g (mole)	AcCl (ml)	Temp (°C)	Time (hr)	TAT % yield	MP (°C)
20 (0.094)	43 (0.421)	0.5	100	0.5	34	134-49
20 (0.094)	43 (0.421)	0.5	100	0.75	47.8	155-8
20 (0.094)	43 (0.421)	0.5	100	1.0	38.4	153-8
20 (0.094)	43 (0.421)	0.5	100	1.75	30.2	153-7
20 (0.094)	43 (0.421)	0.5	100	3.0	25.7	155-8
20 (0.094)	43 (0.421)	3.4	100	0.5	No product	
20 (0.094)	43 (0.421)	0.1	100	2.0	44	150-8
20 (0.094)	43 (0.421)	0	100	2.25	38	155-60
20 (0.094)	43 (0.421)	0	100	26.0	47.8	158-60
10 (0.047)	32 (0.314)	0	110	0.5	68	141-52
10 (0.047)	32 (0.314)	0	110	1.0	60	140-9
10 (0.047)	32 (0.314)	0	110	2.0	61	158-61
10 (0.047)	32 (0.314)	0	110	3.0	71	157-59
10 (0.047)	20 (0.196)	0	110	3.0	67	148-56
10 (0.047)	30 (0.294)	0	110	3.0	71	157-59
10 (0.047)	40 (0.392)	0	110	3.0	69	159-61
10 (0.047)	50 (0.490)	0	110	3.0	74	154-58

*MP of pure TAT is 161°C.

Table 5. Low temperature preparation of TAT

Run	Notebook No.	Solv (ml)	Reactants (mole) A DAPT	B NaAc	C Ac_2O	D AcCl	Mode of addition to solvent	Total time (min)	Temp (°C)	TAT (g)	Yield (%)	MP (°C)
1	762-161-83B	HA_c-100	.047	.19	.28	.094	A: B: C: D: H_2O	135	5-10	12.0	89	153-8
2	762-161-84	HA_c-100	.047	.19	.28	.094	A: B: C: D: H_2O	65	5-10	10.5	78	153-8
3	762-161-85C	HA_c-100	.047	.19	.28	.094	A: B: C: D: H_2O	70	15-20	11.9	88	152-7
4	762-251-18	HA_c-200	.094	.38	.56	.19	A: B: C: D: H_2O	90	5-10	20.5	77	150-7
5	762-161-85B	HA_c-100	.047	.19	.28	.094	A: B: C: D: H_2O	60	10-15	11.5	86	150-7
6	762-161-85A	HA_c-100	.047	.19	.28	.094	A: D: B: C: H_2O	75	10-15	4	30	150-7
7	762-161-83A	HA_c-100	.047	.19	.28	.094	C: A: B: D: H_2O	60	5-10	11.2	83	151-8
8	762-161-86	HA_c-100	.047	.19	.28	.094	A: B: D: H_2O: C	95	10	11.2	83	153-8
9	762-161-84A	HA_c-100	.047	.19	.28	.094	A: D: BH_2O: C	165	10	Unidentified oil		
10	762-161-84B	HA_c-100	.047	.19	.28	.094	A: D: BH_2O: C	75	10	Unidentified oil		
11	762-161-85	HA_c-100	.047	.19	.28	.094	A: D: C: BH_2O	90	10	Unidentified oil		
12	762-161-86A	$CHCl_3$-100	.047	.19	.28	.094	A: B: C: D (No H_2O)	90	5-10	10.8	80	153-8
13	762-251-62	HA_c-100	.047	.19	.374	0	A: B: C: H_2O	135	5-10	Unreacted DAPT		
14	762-251-63	HA_c-100	.047	.19	.374	0	A: B: C: H_2O	135	40	1.6	12	Mainly DAPT
15	762-251-63A	HA_c-100	.047	.19	0	.374	A: B: D: H_2O	135	5-10	1.7	13	Oil-TAT Est by NMR

converted to TAT. Further, it was noted that after the formation of II the acetylation occurred in aqueous media; whereas, prior introduction of water did not yield TAT.

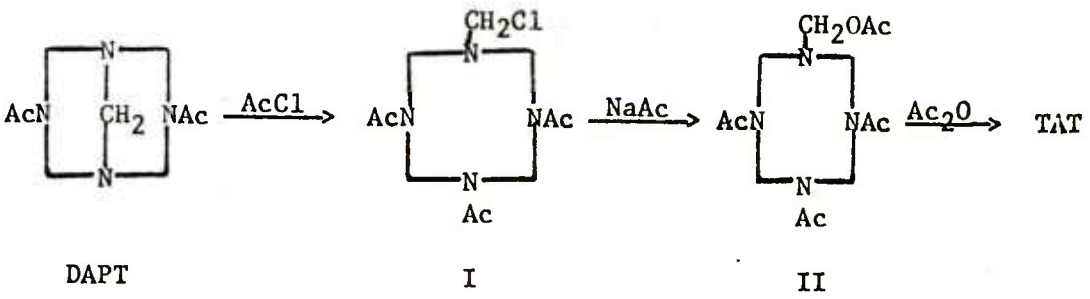


Figure 4. Preparation of TAT with acetyl chloride-acetic anhydride.

Another procedure for the preparation of TAT has been developed by Stanford Research Institute (ref. 29). This involves the reaction of methylenebis-acetamide with paraformaldehyde in refluxing toluene in the presence of catalytic amounts of sulfuric acid. Unfortunately, at this time, yields of only about 20% are attainable.

While purifying TAT we observed that it exists in three polymorphic forms. The infrared spectra and x-ray powder patterns of the forms are different, but their melting points, elemental compositions, and nmr spectra in $DMSO_{d_3}$ and $CDCl_3$ are indistinguishable. The densities of two of the polymorphs were found to be 1.396 g/cm^3 and 1.384 g/cm^3 for Form I and Form II, respectively. The density of Form III has not yet been determined because, on standing for a short time at ambient temperature, it undergoes a solid state transformation to Form I. Form II also undergoes a transformation to I; however, the process is slow. X-ray analysis of Form I (ref. 30) showed that the crystal of 1,3,5,7-tetraceto-1,3,5,7-tetrazacyclooctane, $C_{12}N_4O_4H_{20}$, is tetragonal, a=b= 10.540(2) and c=12.137(3) Å, with four molecules per unit cell. Systematic absences are consistent with space group $P4_12_12$ (enantiomorphous to $P4_32_12$). The structure was solved by direct methods and refined to a final R index R_w=0.037 and R=0.039 for 1244 observed reflections. The molecule consists of alternate CH_2 and N-CO-CH_3 groups in a puckered C-N ring, having a boat shape conformation with a twofold rotation axis through the center of the C-N ring and perpendicular to the mean plane of the puckered ring. The heavy atoms of each acetyl group are essentially coplanar with its neighboring nitrogen atom. The molecular thermal

motion may be represented chiefly by three motions: a libration about the twofold rotation axis and two intramolecular bending motions about the C-C diagonal of the C-N ring.

HMX Synthesis

Attempts to nitrolyze TAT to HMX are also mentioned in reference 17. These unsuccessful attempts included treatment with 100% nitric acid over a range of -30° to +50°C, the use of mixtures of nitric acid, ammonium nitrate,and acetic anhydride at 70°C,and treatment with mixtures of absolute nitric acid and acetic anhydride over the range of 0-25°C. The first two procedures gave no water-insoluble products, while the last gave two unidentified water-insoluble products which were not HMX.

During this investigation, it was established that HMX can be formed from TAT by nitrolysis using nitric acid/P_2O_5, HNO_3/$(CF_3CO)_2O$ or HNO_3/Ac_2O. Nitric acid/P_2O_5 was found to be most efficient (ref. 31). The data for this system are shown in table 6. The data clearly indicate that HMX can be obtained in 80% yield via nitrolysis of TAT with HNO_3/P_2O_5. As indicated in figure 2, four moles of nitric acid are theoretically required to convert TAT to HMX. By using a 34-fold excess of nitric acid containing 33 wt % (nitric acid basis) of P_2O_5, the high yield can be obtained if the nitrolysis is carried out at 70°C for 15 minutes. The reaction proceeds through at least one intermediate, SEX (trinitroacetotetrazacyclooctane), producing gamma HMX with greater than 98% purity. Simple boiling in acetone eliminates the undesirable impurity and converts the gamma isomer into the beta isomer required for military use.

Table 6 also shows that the HMX yield increases with increasing P_2O_5 content. It appears that P_2O_5 does more than just dehydrate the HNO_3. Subsequently, it was found that the actual nitrating species was N_2O_5. This is discussed further under the DADN Process.

Nitric acid/P_2O_5 mixtures have been used as nitrating agents in the past (ref. 32), but it was concluded that they had no special advantages over the more conventional nitrating mixtures. Wyler (ref. 33) used a mixture of HNO_3 and P_2O_5 for nitrolysis of hexamine to RDX. He found that the maximum yield was reached using 25 parts P_2O_5 per 100 parts HNO_3 and that the yield even declined somewhat larger quantities of P_2O_5. However, as shown by the data in table 7, quantities of P_2O_5 exceeding the 25 per 100 ratio are required to achieve high yields of HMX.

Table 6. Nitrolysis of TAT

Wt of TAT: 1 g
Addition temp: 20°C
Heat-up time: 3 min

Run no.	Notebook no.	Conc HNO_3 (%)	Vol HNO_3 (ml)	Additive P_2O_5 (g)	Reaction Conditions temp (°C)	time (min)	Crude HMX (g)	Melting Point[a] (°C)	Purity (%)	Impurities[b]	Pure HMX (g)	Yield (%)
1	762-161-29	100	20	3	70	30	0.78	140-260	50	ATX	0.39	37.5
2	762-161-29-1	100	20	3	70	120	None	---	---	---	---	---
3	762-161-29-C	100	20	3	70	10	0.55	262-267	78	ATX SEX	0.43	41.3
4	762-161-29-D	100	14[c]	2.1	45	30	0.16	219-220	10	SEX	0.015	2.2
5	762-161-7-A	98	20	3	25	150	None	---	---	---	---	---
6	762-161-7-B	98	20	3	70	15	None	---	---	---	---	---
7	762-161-31	95-98	20	3	70	10	None	---	---	---	---	---
8	762-161-31-A	95-98	20	6	70	10	0.38	252-260	70.6	ATX SEX	0.27	25.8
9	762-161-31-B	95-98	20	6	60	10	0.21	217-18	33.4	SEX	0.07	6.7
10	762-161-31-C	95-98	20	6	60	30	0.39	225-260	83.0	SEX	0.32	31.7
11	762-161-31-D	95-98	20	6	60	60	0.63	267-70	76.0	ATX SEX	0.48	46.1
12	762-161-31-E	95-98	20	9	60	30	0.80	267-271	85.0	ATX SEX	0.68	65.4
13	762-161-31-F	95-98	20	12	58	30	0.90	268-272	88.4	ATX SEX	0.80	76.5
14	762-161-31-G	95-98	20	12	50	60	0.90	270-273	91.2	ATX SEX	0.82	79.0
15	762-200-37	95-96	20	10	70	15		273	97	---		70
16	762-200-38-2	95-96	20	10	70	15		273	97	SEX		80
17	762-200-38-3	95-96	20	10	70	15		273	95	SEX		71
18	762-200-39-4	95-96	40	20	70	15		273	97	SEX		70
19	762-200-39-5	95-96	40	20	70	15		274	98	SEX		70
20	762-200-40-6	95-96	20	10	65-70	15		274	98	SEX		77
21	762-200-41-7	95-96	20	10	65-70	15		274	98	SEX		76
22	762-200-42-8	95-96	20	10	68-70	5		245-55		SEX		68
23	762-200-42-9	95-96	20	10	70	5		245-55		SEX		62
24	762-200-43-10	95-96	20	10	70	10		255-65		SEX		71
25	762-200-44-12	95-96	10	10	65-70	15		268-72	90	SEX ATX		65

Table 6 (Continued)

Run no.	Notebook no.	Conc HNO_3 (%)	Vol HNO_3 (ml)	Additive P_2O_5 (g)	Reaction Conditions temp (°C)	Reaction Conditions time (min)	Crude HMX (g)	Melting Point[a] (°C)	Purity (%)	Impurities[b]	Pure HMX (g)	Yield (%)
26	762-200-45-13	95-96	10	10	70	15		268-72	88	SEX ATX		73
27	762-200-45-14	95-96	5	1	70	15		No insoluble products				0
28	762-200-45-14B	95-96	5	1	70	15		No insoluble products				0
29	762-200-46-15	95-96	6	4	62-66	15		Product mainly SEX				0
30	762-200-46-16	95-96	6	4	70	15		250-75	80	SEX		47
31	762-200-45-14A	95-96	5	2	70	15		No insoluble products				0

[a] Melting point of twice rexed HMX by capillary method = 272-274°C.

[b] ATX = $O_2NOCH_2N(NO_2)CH_2N(NO_2)CH_2N(NO_2)CH_2ONO_2$.

[c] 0.7 g cyclooctane used.

Table 7. HMX vs HNO_3-P_2O_5 ratio yield

HNO_3*/P_2O_5 ratio (parts by weight)	HMX (% yield)
100/10	7
100/20	31
100/30	65
100/40	77

*98% nitric acid

Further improvements must be made before the nitrolysis of TAT to HMX becomes fully competitive. Notably, the quantity of HNO_3 required must be reduced as closely as possible to the theoretical four moles. The rapidity of this step (15 minutes as opposed to approximately 1½ hours for the existing process) suggests that the new process could substantially increase the HMX production rate, while reducing the cost.

Nitrolysis of TAT with $HNO_3/(CF_3CO)_2O$ and HNO_3/Ac_2O also produced some HMX. Under the conditions tested so far, the product is generally a mixture of HMX, SEX, and DADN with relatively low HMX content. In addition to the nitrolysis of TAT, attempts were made to prepare HMX from DAPT. Using the P_2O_5/HNO_3 system, found most suitable for TAT nitrolysis, DAPT produced only a 11% yield of HMX.

Although the development of the new route for the preparation of HMX is still at an early stage, some interesting comparisons with the existing process can already be made (table 8). The acetic anhydride consumption thus far attained is 6.3 pounds per pound of hexamine compared to more than 13 pounds required in the existing process. This represents a substantial reduction and, since acetic anhydride is the most costly chemical required for the existing process, representing approximately 25% of the cost of HMX, the reduction could result in considerable savings. Further, it is believed that the anhydride comsumption can be reduced to still lower levels, since the theoretical requirement is only 3 pounds. It is to be expected that, as the acetolysis steps are optimized, the anhydride requirement will approach the theoretical.

Table 8. Comparison of the new synthesis with the present process

		Ac_2O (lb) per lb hexamine	
Acetic anhydride consumption	Present process	13.5	Actual
	New synthesis	6.5	Actual
	New synthesis	3.0	Theory
Methylene yield	Present process	40%	Actual
	Present process	67%	Theory
	New synthesis	41%	Actual
	New synthesis w/o recovery	67%	Theory
	New synthesis w/recovery	100%	Theory

The methylene yield data reveal that the yields obtained in the new process, without recovery of the methylene groups eliminated from hexamine ($(CH_2)_6N_4$) to form the $(CH_2)_4N_4$ ring skeleton, are already equivalent to the yields obtained in the existing process. Since the acetolysis steps (the only steps where methylene groups are eliminated) are relatively straightforward reactions without detectable side reactions, the potential for recovery of the lost methylenes appears good. In the event recovery is successful, the yields would approach the theoretical.

There are several features of the new approach which are unattractive; namely, the use of acetyl chloride (AcCl) in the formation of TAT and the large quantities of nitric acid required for the nitrolysis of TAT to HMX. It is believed, however, that elimination of AcCl and reduction of HNO_3 are surmountable problems. For example, using TAT - High Temperature Method (DAPT : $Ac_2O \rightarrow$ TAT), yields of TAT as high as 70% have already been obtained without the use of AcCl.

The investigations described above have led to the discovery of the first alternative route for the synthesis of HMX. Notwithstanding problems yet to be overcome, it would appear probable that the new

synthesis, with further study, could become competitive with the existing process.

DADN Process

DADN Synthesis

The preparation of DADN was initially carried out in two steps, as indicated by the following scheme:

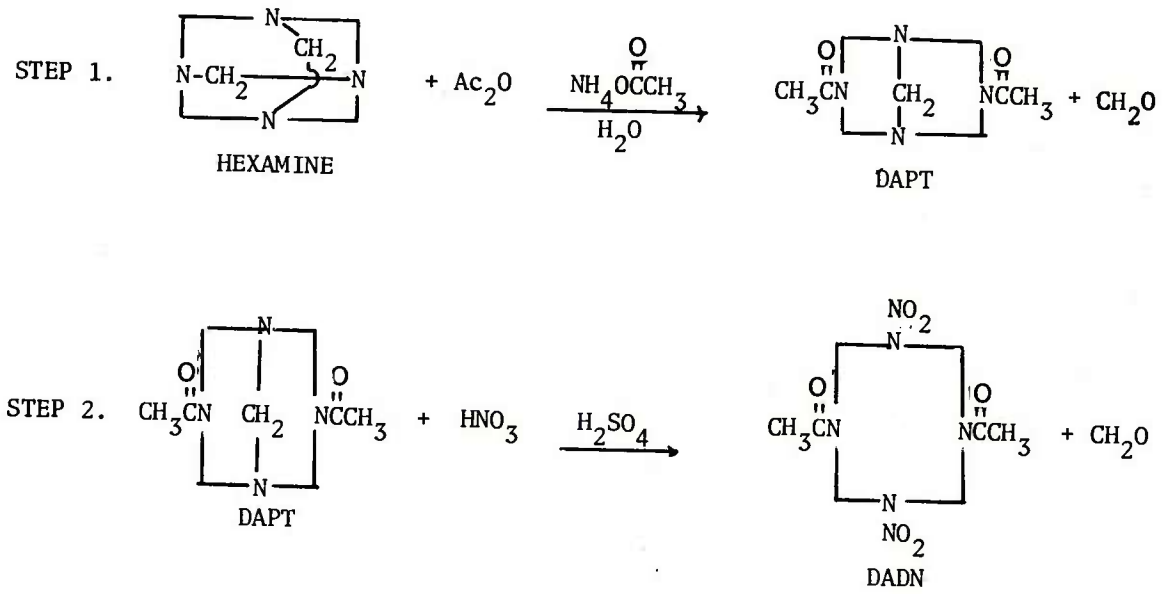


Figure 5. Two-step preparation of DADN

Recently, however, we have found that these two steps could be combined into one operation producing high purity DADN, in excellent yield, without isolation of DAPT. For clarity, the separate steps are discussed first, followed by the experimental results of the combined operation.

Two Step Process

STEP 1. Preparation of Diacetylpentamethylene tetramine (DAPT). The preparation of DAPT was described in the previous section covering the TAT Process.

STEP 2. Preparation of Diacetyldinitrotetraazacyclooctane (DADN) from DAPT. DADN is also a known compound. Its initial preparation reported by Urbanski (ref. 34) and Bachmann (ref. 35) involved the conversion of DAPT to the diacetylnitrosonitro derivative using N_2O_4-HNO_3, followed by persulfate oxidation of the nitroso group to nitro. Thyagarajan (ref. 25,36) recently demonstrated that DADN could be prepared directly from DAPT by reaction of DAPT with nitric-sulfuric mixed acid. He found that absolute nitric acid was not necessary; 70% nitric acid could be used with equally good results. Using a molar ratio, hexamine : HNO_3 : H_2SO_4 of 1: 6.6: 22.5 at ambient temperature produced DADN in 83% yield. This result, especially the fact that the conversion takes place even when water is present, led us to believe that it might be possible to combine Steps 1 and 2 into a one-operation procedure for preparing DADN directly from hexamine without isolating DAPT. This "one operational" procedure is described below.

One Step Process

The preferred reaction procedure is as follows:

Fourteen grams of hexamine (0.1 mole) and 6.2 grams of ammonium acetate (0.08 mole) were added to 7 ml of water at 5-10°C (NH_4Cl-ice cooling bath) contained in a 50-ml flask fitted with a thermometer. To this slurry, which was stirred magnetically, 30.6 grams (0.3 mole) of acetic anhydride was added by drops over a period of 60 minutes while the temperature was maintained between 5 and 10°C. The resulting clear DAPT solution was stirred for 30 minutes, then transferred to an addition funnel and added by drops to a previously prepared mixed acid consisting of 63 grams (1.0 mole) of 99+% HNO_3 and 221 grams (2.26 moles) of 96% H_2SO_4. The addition was carried out over a period of 80 minutes at 18-20°C while the mixture was stirred vigorously with a mechanical stirrer. After the addition was completed, stirring was continued for 20 minutes at 20°C, and then the colorless gassy solution was poured over 1000 grams of ice. The product, which did not separate immediately, was precipitated out by dilution with 1500 ml of water.

After filtration, washing with 5x250 ml of water, and air drying, 27.7 grams of DADN, melting at 265°C, was obtained. The yield, based on hexamine used, was 95% of the theoretical. The nmr ($DMSO_{d6}$) agreed with the assigned structure: $\delta 2.3(S,6,CH_3)$, $\delta 5.56(S,8,CH_2)$.

Anal. calc. for $C_8H_{14}N_6O_6$: C, 33.10; H, 4.86; N, 28.96

Found: C, 33.07; H, 4.95; N, 2923.

The results of four experiments under these conditions are in table 9, below:

Table 9. Preparation of DADN from hexamine (preferred procedure)

Notebook no.	Hexamine (moles)	Temp (°C)	DAPT addition time (min)	DADN (g)	MP (°C)	Purity* (%)	Yield (%)
251-5	0.1	18-20	80	27.7	265	100	95
251-13	0.1	18-20	85	27.8	265	100	96
251-13A	0.1	18-20	85	26.2	264	100	90
251-38	0.3	18-20	75	84.4	265	100	97

*Determined by nmr.

As part of our initial effort in the development of the above procedure, we briefly examined the following:

1. Reduction of nitric acid
2. The use of 70% nitric acid
3. Reduction of sulfuric acid
4. Addition of nitric acid to DAPT-H_2SO_4
5. Effect of stirring

1. Reduction of Nitric Acid

Initially Step 2, the conversion of DAPT to DADN, carried out as a separate operation by Thyagarajan (ref. 25), used a HNO_3 : DAPT molar ratio of 6.6: 1 and produced DADN in approximately 83% yield. In our "one-operation" method, following the procedure and quantities already described, we examined molar ratios of nitric acid to hexamine varying from 10: 1 down to 2.1: 1. The results of this series of experiments are shown in table 10.

Table 10. Reduction of nitric acid

Notebook no.	HNO_3/ hexamine molar ratio	Crude DADN (g)	MP (°C)	Product Composition (%) DANNO	DADN	Yield DADN (%)
251-5	10: 1	27.7	265	0	100	95
219-92	6.6: 1	27.0	265	0	100	93
219-92-1	3.3: 1	27.4	255	4	96	91
219-93-2	2.7: 1	25.4	250	11	89	78
219-94	2.1: 1	19.7	250	8	92	63

In this series of experiments, an exothermic reaction occurred prior to the completion of the DAPT addition when nitric acid to hexamine ratios of 3.3, 2.7, and 2.1: 1 were used. At the 6.6: 1 ratio the exotherm occurred during the aging period, while at 10: 1 no exotherm was evident. The formation of DANNO (1,5-diacetyl-3-nitro-7-nitroso-1,3,5,7-tetraazacyclooctane) appears to be associated with this exothermic reaction and probably results from the reaction of oxides of nitrogen, liberated during the exotherm, with DAPT (ref. 35). The highest yields of pure DADN are obtained at HNO_3/hexamine ratios >6.6: 1. Using ratios >6.6: 1 prevents the exothermic reaction from occurring during the DAPT addition and thereby eliminates the formation of DANNO as an impurity. It therefore appears that it may not be possible to reduce the quantity of nitric acid below the 6.6 level.

2. Use of 70% Nitric Acid

Concurrent to our experiments concerning the reduction of 99+% nitric acid,we briefly examined the use of 70% nitric acid at HNO_3/ hexamine ratios of 6.6, 3.3, and 2.7: 1, respectively. The results are shown in table 11.

Table 11. Reduction of 70% nitric acid

Notebook no.	HNO_3/ hexamine molar ratio	Crude DADN (g)	MP (°C)	Product Composition (%) DANNO	DADN	Yield DADN (%)
219-92-2	6.6	27.5	260	3	97	92
219-93	3.3	27.5	255	7	93	88
219-93-1	2.7	25.9	250	11	89	79.6

On comparing the 70% nitric data with the 99+% nitric data (table 10),the results appear to be almost identical. There is a slight increase in DANNO content at 6.6 and 3.3: 1 nitric/hexamine ratios; however, these differences could be due to slight changes in reaction conditions (temp., addition time, etc.) which could not be accurately controlled.

3. Reduction of Sulfuric Acid

A number of experiments were conducted at a reduced sulfuric acid level in which the H_2SO_4/hexamine molar ratio was reduced from 22.5: 1 to 11.2: 1. The reactions were carried out at different HNO_3/ hexamine ratios using both 99+% HNO_3 and 70% HNO_3. The results are shown in table 12.

Table 12. Reduction of sulfuric acid

Notebook no.	Sulfuric hexamine molar ratio	Nitric/ hexamine molar ratio	Nitric acid (%)	Crude DADN (g)	MP (°C)	Prod comp (%) DANNO	DADN	Yield DADN (%)
219-99	11.2	10:1	99+	25	254	7	93	80
219-96	11.2	6.6:1	99+	25.7	254	13	87	77
219-97	11.2	3.3:1	99+	24.8	250	16	84	72
219-97A	11.2	6.6:1	70	21.8	244	25	73	55
219-98	11.2	3.3:1	70	21.2	244	25	73	55

In studying this table and comparing the data that tabulated at the 22.5 sulfuric/hexamine level shown in tables 10 and 11, it becomes quite evident that reduction of sulfuric is detrimental. The yields drop off considerably and, in all cases, the DANNO content increases. Furthermore, in this series of reactions the exothermic reaction occurred prior to completion of the DAPT addition. Also evident is the reduction in DADN yield and the increase in DANNO as a function of the type of nitric acid used. It would appear that water has a detrimental effect.

4. Addition of Nitric Acid to DAPT-H_2SO_4

In one experiment, the DAPT solution was added to sulfuric acid, then nitric acid was added to the resulting DAPT-H_2SO_4 solution. In this experiment a 6.6:1 70% HNO_3/hexamine was used, the sulfuric acid/hexamine ratio was 22.5:1 and the addition temperature for both nitric and DAPT addition was 15-20°C. The yield of DADN was only 43%, and the product melted at 260°C.

The standard run (see table 11, Notebook No. 219-92-2) gave 92% yield of DADN.

5. Effect of Stirring

In early experiments, a magnetic stirring bar was used to agitate the HNO_3-H_2SO_4 mixture during DAPT addition. This type of agitation comprised slow swirling as opposed to the rapid-swirling-splashing agitation produced by stirring vigorously with a mechanical

stirrer. Although the reaction vessel was of the same capacity as the vessel used in later experiments using mechanical stirring and the reaction conditions were essentially the same described in our preferred procedure, the yields of DADN were 10 to 20% lower than the yields obtained in experiments using mechanical stirring. The lower yield can probably be attributed to the vigorous nature of the exothermic reaction. This reaction in all cases occurred sooner and in many experiments was so vigorous that the contents of the flask framed out of the reaction vessel. Temperatures as high as 160°C were observed in some experiments. This difficulty was overcome, however, by use of vigorous mechanical stirring.

At this point, it was thought that the exploratory development of Stage I of the DADN process was essentially complete. However, in order for the new HMX process to become competitive with the Bachmann process, which is currently used for the manufacture of HMX, a number of improvements must be incorporated into Stage I: "The Preparation of DADN." In any process improvement study we would suggest that the highest priority be given to:

1. Reducing overall reaction time from 3 hours to approximately 1½ hours or less.

2. Developing a simplified DADN isolation procedure which provides for separating and recycling of HNO_3, H_2SO_4, and CH_3COOH acids.

Other recommendations which deserve attention, but at a lower priority, include:

1. Analyzing any hazards that might be present in the DADN process, including the characterization of the explosive properties of DADN.

2. Developing a system for recovery of the formaldehyde values liberated during acetolysis and nitration phases.

3. Eliminating the refrigeration requirement present in the existing DADN procedure (i.e., operating above 10°C).

4. Determining the possibility of reverse additions.

5. Considering the feasibility of a continuous DADN process.

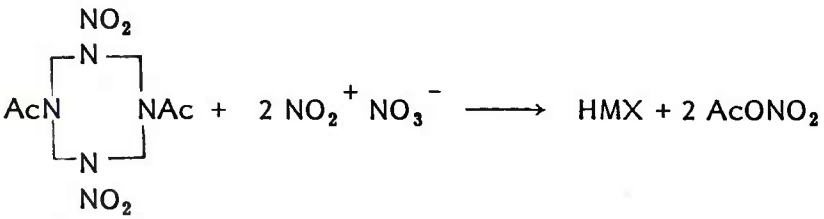
Advanced development was continued at the Los Alamos Scientific Laboratory. LASL's efforts are covered later in this report.

HMX Synthesis

Several nitrating systems for the nitrolysis of DADN have been investigated and the data compiled as of this date are given in tables 13 through 18. The systems examined are as follows:

System	Table
1. TFAA - HNO_3 in nitric acid	13
2. TFAA - HNO_3 in nitromethane and other solvents	14
3. PPA - HNO_3 in PPA	15
4. P_2O_5 - HNO_3 in nitric acid	16
5. SO_3 - HNO_3 in nitric acid	17
6. N_2O_5 in nitric acid and other solvents	18

In recording these data, it has been assumed that N_2O_5 is the source of nitronium ions, with the nitrolysis equation as follows:



The required nitric acid is,therefore,reported in terms of N_2O_5 stoichiometry rather than HNO_3. This assumption has some experimental support since in two experiments, one (run 251-49, table 14) using HNO_3 in nitromethane and another (run 271-70, table 18) using N_2O_5 in nitromethane, HMX was only produced when N_2O_5 was the nitrating source. Further research, however, is necessary to establish whether this assumption is entirely valid, since in some experiments using HNO_3 small yields of HMX are observed.

Trifluoroacetic Anhydride - Nitric Acid in Excess Nitric Acid

Trifluoroacetic anhydride has been shown to dehydrate nitric acid to produce nitrogen pentoxide (ref. 37) by the following equation:

$$(CF_3CO)_2O + 2HNO_3 \xrightarrow{H_2O} NO_2^+ NO_3^- + 2CF_3COOH$$

In the experiments conducted in this section, DADN was insoluble if stoichiometric quantities of TFAA and HNO_3 were used. DADN was also insoluble in trifluoroacetic acid, which is the product formed during the preparation of N_2O_5. This difficulty was overcome, however, by using excess nitric acid as the solvent medium; clear solutions resulted. However, as the reaction proceeded, precipitation began to occur in approximately 10 to 15 minutes. The products isolated by quenching the reaction mixture on ice. In these experiments, 3 grams of DADN were used. The stoichiometric qunatity of N_2O_5 was assumed to be 2 moles, or 2.24 grams. The data are given in table 13.

Although somewhat scattered and preliminary, the data obtained for this nitrolysis system do indicate that the system is capable of producing HMX in yields of at least 75 to 80% of the theoretical. The data also suggest that considerably more than the stoichiometric quantity of N_2O_5 is required to achieve the higher yields. This is probably due to the instability of N_2O_5 at the temperatures required for rapid DADN reaction and/or the very fluid nature of the reaction system which allows the N_2O_5 to escape faster than reaction is occurring.

Another aspect to be considered is the drastic drop in crude yield at 70°C. This indicates that one of the three components or all three (HMX, SEX, DADN) are somewhat unstable at elevated temperatures when in contact with this nitrolysis system. This is discussed in a later section of this report. Although the data obtained in temperature staging experiments are incomplete, there appears to be a trend to higher yields.

At the present time,if the best run (251-41A) were put into production, the requirements would be 21 pounds HNO_3 and 13.2 pounds of TFAA to produce 1 pound HMX.

Table 13. TFAA-HNO_3 in nitric acid[a]

Notebook no.	N_2O_5[b]	Temp (°C)	Time (min)	Yield crude (%)	Purity (%)	Yield HMX (%)	Product composition (%) HMX	SEX	DADN	Acid composition (g) N_2O_5	HNO_3	TFA
251-31	2.0	70	10	24.5	85	21	85	15	0	4.7	24.5	9.9
251-30-1	2.0	60	22	67	83	56	83	11	6 ATX	4.7	24.5	9.9
251-32-2	2.0	50	60	74	89	65	89	11	0	4.7	24.5	9.9
251-32	2.0	50	45	77	88	67	88	12	0	4.7	24.5	9.9
251-32-1	2.0	45	45	75	49	37	49	51	0	4.7	24.5	9.9
251-30	3.15	60	22	65	87	57	87	13	0	7.05	36.8	14.9
251-28	4.6	58	22	75	79	60	79	21	0	10.2	18.1	21.6
251-33	4.6	50	60	79	90	70	90	10	0	10.2	18.1	21.6
351-39	4.6	50	60	82	90	73	90	10	0	10.2	18.1	21.6
251-27	4.6	50	45	75	88	66	88	12	0	10.2	18.1	21.6
251-24	6.3	54	22	72	85	61	85	15	0	14.1	28.5	29.7
251-40	6.3	50	60	82	93	76	93	7	0	14.1	28.5	19.7
					Temperature staging experiments[c]							
251-27-1	4.6	70 60	15 30	65	88	57	88	3	9 ATX	10.2	18.1	21.6
251-40A	4.6	30 50	30 30	88	78	68	78	22	0	10.2	18.1	21.6
251-40B	6.3	30 30	30 30	85	86	73	86	14	0	14.1	28.51	29.7
251-41B	6.3	10 50	30 60	85	92	78	92	8	0	14.1	28.51	29.7
251-41	6.3	20 50	30 60	85	94	80	94	6	0	14.1	28.51	29.7
251-41A	6.3	35 50	30 60	86	95	81.5	95	5	0	14.1	28.51	29.7

[a] 3 grams DADN used.

[b] Temperature and corresponding time shown for each of two stages.

[c] Multiple of stoichiometric requirement used.

Trifluoroacetic Anhydride - Nitric Acid in Nitromethane and Other Solvents

In this series of experiments, an effort was made (1) to determine whether nitric acid in excess played any role in the nitration of DADN, (2) whether other solvents could be substituted for nitric acid to solubilize DADN, and (3) to optimize any system that was found promising. The data are compiled in table 14.

From the data presented in table 14, it is evident that these objectives have been achieved. Comparison of run 251-49 (no N_2O_5) with run 251-51-3 (no HNO_3) shows conclusively that N_2O_5 is the nitrating agent. No HMX is obtained unless N_2O_5 is present in the nitrating medium. It was also found that nitromethane can be used as a reaction solvent in place of nitric acid. This is the only solvent found thus far to solubilize DADN. In both the chloroform and acetonitrile systems, DADN remained insoluble. As a consequence, little or no nitration occurred. Yields of HMX of approximately 90% can be expected for the nitrolysis reaction in nitromethane. It appears, however, that approximately eight stoichiometric quantities of N_2O_5 are required to nitrate DADN in reasonable lengths of time. This system would require 7.5 pounds HNO_3, 12.5 pounds TFAA, and 10 pounds CH_3NO_2 to produce 1 pound HMX. On a DADN basis, 1 pound would require 7 pounds HNO_3 and 11.5 pounds TFAA. There is one obstacle to this system which may hinder its utilization: During the course of nitrolysis, some nitroform is produced, but no attempt has been made to determine the extent of this secondary reaction. Again, during nitrolysis, HMX precipitates out which could simplify its separation.

Polyphosphoric Acid - Nitric Acid in Polyphosphoric Acid

This nitrolysis system appears to be the most promising of those tested from the standpoint of practicability (table 15). Initially (runs 248-100 through 248-55) only low yields of HMX could be obtained; however, after examining the DuPont report (ref. 14) describing the nitrolysis of TRAT with PPA-HNO_3, it was noted that C. Rolston was able to obtain high yields of pure RDX only by using PPA-HNO_3 mixtures having approximately 80 weight % PPA. Our data at 35 and 52 weight % PPA parallel the DuPont data at reduced PPA levels: yields of HMX in the order of 30 to 60% were noted. At the higher level of approximately 70 weight % PPA, it was immediately found that pure HMX could be prepared in yields

Table 14. TFAA-HNO_3 in nitromethane and other solvents[a]

Notebook no.	N_2O_5[b]	Solv (ml)	Temp (IC)	Time (min)	Crude yield (%)	Purity (%)	HMX yield (%)	Product composition (%) HMX	SEX	DADN	Acid composition, g N_2O_5	HMO_3	TFA	System
251-49	0	CH_3NO_2 (25)	50	60	80	0	0	0	0	100	0	10.5	0	
251-43	2	$CHCl_3$ (50)	50	60	67	0	0	0	0	100	4.5	5.2	9.5	Hetero
251-46	2	CH_3CN (50)	50	120	86	21	18	21	11	68	4.5	5.2	9.5	Hetero
251-47	2	CH_3CN (25)	60	60	83	17	14	17	11	72	4.5	5.2	9.5	Hetero
251-50	2	CH_3NO_2 (25)	50	5	91	39	35	39	29	32	4.5	5.2	9.5	Homo
251-50	2	CH_3NO_2 (25)	50	15	87	56	49	56	27	17	4.5	5.2	9.5	Homo
251-50	2	CH_3NO_2 (25)	50	30	83	62	52	62	21	17	4.5	5.2	9.5	Homo
251-50	2	CH_3NO_2 (25)	50	45	85	62	53	62	24	14	4.5	5.2	9.5	Homo
251-50	2	CH_3NO_2 (25)	50	60	84	65	54	54	18	16	4.5	5.2	9.5	Homo
251-51-4	4	CH_3NO_2 (25)	50	5	89	66	59	66	22	11	9.0	0	19.0	
251-51-2	4	CH_3NO_2 (25)	50	15	88	76	67	76	14	10	9.0	0	19.0	
251-51-1	4	CH_3NO_2 (25)	50	30	87	78	68	78	13	9	9.0	0	19.0	

Table 14 (Continued)

Notebook no.	N_2O_5 [b]	Solv (ml)	Temp (IC)	Time (min)	Crude yield (%)	Purity (%)	HMX yield (%)	Product composition (%) HMX	SEX	DADN	Acid composition, g N_2O_5	HMO_3	TFA	System
251-51-3	4	CH_3NO_2 (25)	50	45	88	75	66	75	25	0	4.5	9.0	0	
251-52-1	4	CH_3NO_2 (25)	60	5	86	68	59	68	18	14	9.0	0	19.0	
251-52	4	CH_3NO_2 (25)	60	15	85	68	58	68	19	13	9.0	0	19.0	
251-52-2	4	CH_3NO_2 (25)	70	5	82	60	49	60	27	13	9.0	0	19.0	
251-55	4	CH_3NO_2 (25)	40	5	89	36	32	36	28	35	9.0	0	19.0	
251-54-3	4	CH_3NO_2 (25)	40	15	91.5	69	63	69	23	8	9.0	0	19.0	
251-54-2	4	CH_3NO_2 (25)	40	30	91.2	79	72	79	21	0	9.0	0	19.0	
251-54-1	4	CH_3NO_2 (25)	40	45	90.5	86	78	86	14	0	9.0	0	19.0	
251-54	4	CH_3NO_2 (25)	40	60	91.6	88	80.5	88	12	0	9.0	0	19.0	
251-55-1	4	CH_3NO_2 (25)	40	75	91.0	90.5	82.4	90.5	9.5	0	9.0	0	19.0	
251-55-2	4	CH_3NO_2 (25)	40	90	90.3	90.5	81.6	90.5	9.5	0	9.0	0	19.0	
251-55-4	4	CH_3NO_2 (25)	40	60	92.3	86	79.5	86	14	0	9.0	0	19.0	

Table 14 (Continued)

Notebook no.	N_2O_5[b]	Solv (ml)	Temp (IC)	Time (min)	Crude yield (%)	Purity (%)	HMX yield (%)	Product composition (%) HMX	SEX	DADN	Acid composition, g N_2O_5	HMO_3	TFA	System
251-58	4	CH_3NO_2 (25)	35	60	93.2	90.5	85	90.5	9.4	0	9.0	0	19.0	
251-58-2	4	CH_3NO_2 (25)	25	60	94	73	69	73	17	10	9.0	0	19.0	
251-55-3	6	CH_3NO_2 (25)	40	60	94	94	88	94	6	0	13.4	0	28.5	
251-58-1	6	CH_3NO_2 (40)	40	60	91.5	93.5	86	93.5	6.5	0	13.4	0	28.5	
251-59-2	6	CH_3NO_2 (25)	40	90	91.5	93.5	86	93.5	6.5	0	13.4	0	28.5	
251-56-1	8	CH_3NO_2 (25)	40	60	93	94	87	94	6	0	17.9	0	38.1	
251-58-2	8	CH_3NO_2 (25)	40	75	91	97	88	97	3	0	9.0	0	19.0	
251-59-2	8	CH_3NO_2	40	90	93.5	97	91	97	3	0	9.0	0	19.0	
				Temperature Staging[c]										
251-59	4	CH_3NO_2 (25)	25 50	30 30	90.6	85.6	77.5	85.6	11.2	3.2	9.0	0	18.0	
251-56	6	CH_3NO_2 (25)	40 50	45 15	94	94	88.5	94	6	0	13.4	0	28.5	

Table 14 (Continued)

Notebook no.	N_2O_5[b]	Solv (ml)	Temp (IC)	Time (min)	Crude yield (%)	Purity (%)	HMX yield (%)	Product composition (%) HMX	SEX	DADN	Acid composition, g N_2O_5	HMO_3	TFA	System
251-52-1	4	CH_3NO_2 (25)	60	5	86	68	59	68	18	14	9.0	0	19.0	
251-52	4	CH_3NO_2 (25)	60	15	85	68	58	68	19	13	9.0	0	19.0	
251-52-2	4	CH_3NO_2 (25)	70	5	82	60	49	60	27	13	9.0	0	19.0	
251-55	4	CH_3NO_2 (25)	40	5	89	36	32	36	28	35	9.0	0	19.0	
251-54-3	4	CH_3NO_2 (25)	40	15	91.5	69	63	69	23	8	9.0	0	19.0	
251-54-2	4	CH_3NO_2 (25)	40	30	91.2	79	72	79	21	0	9.0	0	19.0	
251-54-1	4	CH_3NO_2 (25)	40	45	90.5	86	78	86	14	0	9.0	0	19.0	
251-54	4	CH_3NO_2 (25)	40	60	91.6	88	80.5	88	12	0	9.0	0	19.0	
251-55-1	4	CH_3NO_2 (25)	40	75	91.0	90.5	82.4	90.5	9.5	0	9.0	0	19.0	
251-55-2	4	CH_3NO_2 (25)	40	90	90.3	90.5	81.6	90.5	9.5	0	9.0	0	19.0	
251-55-4	4	CH_3NO_2 (25)	40	60	92.3	86	79.5	86	14	0	9.0	0	19.0	

Table 14 (Continued)

Notebook no.	N_2O_5[b]	Solv (ml)	Temp (IC)	Time (min)	Crude yield (%)	Purity (%)	HMX yield (%)	Product composition (%) HMX	SEX	DADN	Acid composition, g N_2O_5	HMO_3	TFA	System
251-58	4	CH_3NO_2 (25)	35	60	93.2	90.5	85	90.5	9.4	0	9.0	0	19.0	
251-58-2	4	CH_3NO_2 (25)	25	60	94	73	69	73	17	10	9.0	0	19.0	
251-55-3	6	CH_3NO_2 (25)	40	60	94	94	88	94	6	0	13.4	0	28.5	
251-58-1	6	CH_3NO_2 (40)	40	60	91.5	93.5	86	93.5	6.5	0	13.4	0	28.5	
251-59-2	6	CH_3NO_2 (25)	40	90	91.5	93.5	86	93.5	6.5	0	13.4	0	28.5	
251-56-1	8	CH_3NO_2 (25)	40	60	93	94	87	94	6	0	17.9	0	38.1	
251-58-1	8	CH_3NO_2 (25)	40	75	91	97	88	97	3	0	9.0	0	19.0	
251-59-2	8	CH_3NO_2 (25)	40	90	93.5	97	91	97	3	0	9.0	0	19.0	
					Temperature staging[c]									
251-59	4	CH_3NO_2 (25)	25 50	30 30	90.6	85.6	77.5	85.6	11.2	3.2	9.0	0	18.0	
251-56	6	CH_3NO_2 (25)	40 50	45 15	94	94	88.5	94	6	0	13.4	0	28.5	

[a] 3 grams DADN used.

[b] Multiple of stoichiometric requirement used.

[c] Temperature and corresponding time shown for each of two stages.

Table 15. Polyphosphoric acid - HNO_3 in polyphosphoric

Notebook no.	DADN (g)	HNO_3 (g)	PPA (g)	Wt % PPA	N_2O_5*	Temp (°C)	Time (min)	Crude yield (%)	Purity (%)	HMX yield (%)	MP (°C)	Product composition (%) HMX	SEX	DADN	Acid composition (g) N_2O_5	PPA	H_3PO_4	HNO_3
248-100	5	37.4	20	35	7.2	70	5	66	51	34	223	51	2	2	26.8	0	24.5	5.9
248-36	5	37.4	20	35	7.2	70	15	69	83	57	245	83	17	0	26.8	0	24.5	5.9
248-37	5	37.4	20	35	7.2	70	30	39	100	39	276	100	0	0	26.8	0	24.5	5.9
248-34	5	37.4	20	35	7.2	60	15	77	39	30	227	39	30	31	26.8	0	24.5	5.9
248-51	5	37.4	20	35	7.2	60	15	80	37	30	240	37	21	42	26.8	0	24.5	5.9
248-35	5	37.4	20	35	7.2	60	30	69	68	47	225	68	32	0	26.8	0	24.5	5.9
248-53	5	37.4	20	35	7.2	50	50	80	42	34	230	42	32	28	26.8	0	24.5	5.9
248-46	1	45	0	0	0	70	15	38	--	--	230	--	--	--	0	0	0	45
248-57	5	37.4	40	52	8.6	70	15	67	70	47	226	70	20	10	32	16.3	29	0
248-61	5	37.4	40	52	8.6	70	30	68	82	56	273	82	18	0	32	16.3	29	0
248-55	5	37.4	40	52	8.6	60	15	87	37	32	240	37	21	42	32	16.3	29	0
258-27	3.1	45	100	69	17.2	60-70	60	86	100	86	--	100	0	0	39.6	71.4	35	0
258-28	2.8	45	100	69	18.4	60-70	60	81	100	81	--	100	0	0	38.4	71.4	35	0
258-29	3.06	22.5	50	69	8.5	60-70	60	97	100	97	--	100	0	0	19.4	35.7	17.5	0
258-30	3.1	22.5	50	69	8.4	60-70	60	94	100	94	--	100	0	0	19.4	35.7	17.5	0
258-31	3.1	22.5	50	69	8.4	60-70	60	95	100	95	--	100	0	0	19.2	35.7	17.5	0
258-32	2.52	22.5	50	69	10.2	60-70	60	99	100	99	--	100	0	0	19.2	35.7	17.5	0
258-33	2.93	22.5	50	69	8.8	60-70	60	99	100	99	--	100	0	0	29.2	35.7	17.5	0
258-34	6.0	22.5	50	69	4.3	60-70	60	92	100	92	--	100	0	0	19.2	35.7	17.5	0
258-35	6.12	22.5	50	69	4.24	60-70	60	88	100	88	--	100	0	0	19.2	35.7	17.5	0
258-36	6.12	22.5	50	69	4.45	60-70	60	94	100	94	--	100	0	0	19.2	35.7	17.5	0
258-37	8.92	22.5	50	69	2.9	60-70	60	88	100	88	--	100	0	0	19.2	35.7	17.5	0
258-39	9.1	22.5	50	69	2.84	60-70	45	83	93	77	--	93	7	0	19.2	35.7	17.5	0
258-40	8.8	22.5	50	69	2.94	60-70	60	89	955	85	--	95.5	4.7	0	19.2	35.7	17.5	0
258-41	7.6	22.5	50	69	3.4	60-70	60	84	100	84	--	100	0	0	19.2	35.7	17.5	0
258-42	7.76	22.5	50	69	3.3	60-70	60	84	100	84	--	100	0	0	19.2	35.7	17.5	0
258-43	7.5	22.5	50	69	3.4	60-70	30	86	86	74	--	86	14	0	19.2	35.7	17.5	0
258-44	2.83	22.5	50	69	9.1	60-70	60	99	100	99	--	100	0	0	19.2	35.7	17.5	0
258-45	6.97	22.5	50	69	3.7	60-70	60	83	96.5	80	--	96.5	3.5	0	19.2	35.7	17.5	0
258-38	2.88	22.5	50	69	8.0	60-70	30	96	100	96	--	100	0	0	19.2	35.7	17.5	0

*Multiple of stoichiometric requirement used.

of 81-99%. A clue as to why high percentages of PPA are required may be found in the nature of the acid composition. If one assumes that PPA is $H_2P_2O_6$ or H_2O/P_2O_5 = 1:1 based on equation $P_2O_5 + 2HNO_3$ $(-H_2O)$ $N_2O_5 + 2HPO_3$ (a reasonable assumption since the molar ratio H_2O/P_2O_5 = 1.08:1 in 88% PPA) and further that $HPO_3 + 2HNO_3$ $(-H_2O)$ $N_2O_5 + H_3PO_4$ is the equation describing the nitrolysis of DADN in the PPA-HNO_3 system, it is immediately observed that at low weight % PPA, H_3PO_4 is in excess over unreacted PPA. Only at weight % > 52% is the ratio reversed. It may well be that H_3PO_4 acts to inhibit the reaction.

More extensive work on this system must be carried out; however, on the basis of run 258-35, it would presently require 4.1 pounds HNO_3 and 9 pounds of PPA to produce 1 pound of HMX.

Further work on this system is reported in the Advanced Development Section of this report.

Phosphorous Pentoxide - Nitric Acid in Excess Nitric Acid

Very little systematic effort has been made in the past by others to develop this system due to the impracticality of the use of P_2O_5. As in other nitrolysis systems studied by us to date, i.e., with TAT and TRAT, excellent HMX-RDX yields are attainable with DADN using the P_2O_5-nitric system (table 16).

Sulfur Trioxide - Nitric Acid in Nitric Acid

This system can be used to prepare HMX from DADN, but the HMX yields are only 40-60% (table 17). For the purpose of calculating N_2O_5 available, it was assumed that the equation was $SO_3 + 2HNO_3 \rightarrow N_2O_5 + H_2SO_4$; however, this reaction is not that simple, as the literature abounds with complex nitronium salts prepared by interaction of SO_3 and HNO_3. The biggest single drawback to this system, however, is probably the instability of nitramines (DADN, SEX, and HMX) in H_2SO_4 at elevated temperatures as indicated by the low crude yields at 60-70°C. Again, however, it may be that a very high weight % SO_3 is required to achieve HMX in high yield.

Table 16. Phosphorous pentoxide - nitric acid in nitric acid

Notebook no.	DADN (g)	HNO_3 (g)	P_2O_5 (g)	Wt % PPA	N_2O_5*	Temp (°C)	Time (min)	Crude yield (%)	Purity (%)	HMX yield (%)	Product composition (%) HMX	SEX	DADN	Acid composition (g) N_2O_5	H_3PO_4	HNO_3
231-38	69	30	0	0	0	50	15	50	88	44	88	12	0	0	0	30
231-39	0.99	30	0	0	0	50	50	40	--	--	--	--	--	0	0	30
248-45	1	White 45	0	0	0	70	15	18	98	17.6	98	2	0	0	0	45
248-46	1	Red 45	0	0	0	70	15	38	60	23	60	--	--	0	0	45
231-35	0.80	30	10	25	38.4	70	15	90.4	100	90.4	100	0	0	22.9	13.8	3.3
231-36	0.82	30	10	25	37.3	25	60	86	0	0	0	0	100	22.9	13.8	3.3
231-32	0.89	30	10	25	34.4	65	15	97.5	100	97.5	100	0	0	22.9	13.8	3.3
231-37	1.19	30	10	25	25.8	50	50	98.7	100	98.7	100	0	0	22.9	13.8	3.3
248-47	1	37.6	10	21	30.8	50	15	81.5	90	74	90	10	0	22.9	13.8	10.9
248-48	1	37.6	10	21	30.8	60	15	81.4	100	81.4	100	0	0	22.9	13.8	10.9
248-49	1	37.6	10	21	30.8	50	50	97	100	97	100	0	0	22.9	13.8	10.9
248-23	2	30	10	25	15.4	60	10	82	54	44	54	--	--	22.9	13.8	3.3
271-42	3	22.5	6	21	6.1	50	60	88	93	82	93	7	0	13.6	8.2	6.6

*Multiple of stoichiometric requirement used.

Table 17. Sulfur trioxide-nitric acid in nitric acid

Notebook no.	DADN (g)	HNO_3 (g)	SO_3 (g)	Wt % SO_3	N_2O_5*	Temp (°C)	Time (min)	Crude yield (%)	Purity (%)	HMX yield (%)	Product composition (%) HMX	SEX	DADN	Acid composition (g) N_2O_5	HNO_3	H_2SO_4	SO_3
248-98	3	30	4.6	13.3	2.77	60	15	58	72	42	72	18	10	6.2	11.75	5.6	0
248-99	3	30	9.3	23.6	5.6	70	15	8	100	8	100	0	0	12.5	15.4	11.4	0
248-97	3	30	9.3	23.6	5.6	60	15	53	85	45	85	15	0	12.5	15.4	11.4	0
248-88	3	30	9.3	23.6	5.6	60	15	65	77	50	77	23	0	12.5	15.4	11.4	0
248-85	3	30	9.3	23.6	5.6	60	15	60	80	48	80	20	0	12.5	15.4	11.4	0
248-86	3	30	9.3	23.6	5.6	60	5	75	53	40	53	22	25	12.5	15.4	11.4	0
248-65	3	30	9.3	23.6	5.6	47	70	68	89	60	89	11	0	12.5	15.4	11.4	0
248-82	3	30	9.3	23.6	5.6	47	60	66	43	28	43	33	24	12.5	15.4	11.4	0
248-87	3	30	9.3	23.6	5.6	50	15	84	37	33	37	35	25	12.5	15.4	11.4	0
248-64	3	30	9.3	23.6	5.6	27	120	89	50	44.5	50	--	--	12.5	15.4	11.4	0
248-67	3	30	29.7	50	11.4	24	120	91	28	25	28	25	47	25.7	0	23.4	10.6
248-80	3	30	29.7	50	11.4	47	60	48	76	36	76	24	0	25.7	0	23.4	10.6

*Multiple of stoichiometric requirement used.

Nitrogen Pentoxide in Nitric Acid and Other Solvents

The data compiled for this system are preliminary and further work is required to obtain high yields of HMX. At this time, however, the data indicate that HMX can be prepared in at least 80% yield. Run 271-39-1 (table 18) definitely shows that this system has promise for the future. In this run, the lowest N_2O_5 stoichiometry of all systems was used and the yield of HMX was 82%. A kinetic analysis (ref. 38) of the data indicated that the reaction proceeded DADN $\xrightarrow{k_1}$ SEX $\xrightarrow{k_2}$ HMX and that the rate constants, k_1 and k_2, were about equal. Recycle of the acid appears to be straightforward and similar to that of the nitric acid-RDX processes. Although a convenient large-scale process for producing N_2O_5 has yet to be developed, the data suggest that this system may be the cheapest system for the preparation of HMX. A long range effort to develop an economical procedure for the preparation of N_2O_5 from NO_2, O_2 and NO is currently being conducted at Stanford Research Institute under the sponsorship of the Army Research Office (ref. 39).

The following recommendations were used as the basis for the advanced development studies which are reported in the advanced development section of this report:

1. Optimize the PPA-HNO_3-DADN system via a complete parametric study.

2. Re-estimate the cost of the process using the latest LASL and ARRADCOM Data.

3. Scale-Up PPA-HNO_3-DADN system and develop procedures for HMX separation and acid recycle. Study the isolation of HMX from the PPA-HNO_3-DADN system with aim of isolating only acid-free β HMX, thereby eliminating recrystallization.

4. Develop purity determination procedures.

5. Study polyphosphoric acid regeneration and recycle.

Table 18. Nitrogen-pentoxide in nitric acid and other solvents

Notebook no.	DADN (g)	HNO_3 (g)	Solv (ml)	N_2O_5 (g)	N_2O_5 wt %	N_2O_5 [a]	Temp (°C)	Time (min)	Crude yield (%)	HMX yield (%)	Product composition (%) HMX	SEX	DADN
271-9	3	30	--	10	25	4.5	50	45	62	42	67	33	0
271-11	3	30	--	15	33	6.7	50	15	85	20	24	73	3
271-17	3	23.7	--	6.3	21	2.8	50	50	56	45	80	8	--
271-17-1	3	23.7	--	6.3	21	2.8	70	15	65	40	61	39	0
271-17-2	1	11.8	--	3.16	21	4.25	25	24 hr	73	68	93	7	0
271-27-1	3	37	--	0	0	0	25	24 hr	43	40	94	6	0
271-21	3	18	--	12	40	5.35	50	50	58	41	70	30	0
271-41	3	18.5	--	4	18	1.8	50	5	90	21	23	28	49
271-39	3	18.5	--	4	18	1.8	50	15	84	47	56	30	14
271-41-1	3	18.5	--	4	18	1.8	50	30	88	72	82	15	3
271-39-1	3	18.5	--	4	18	1.8	50	60	87	82	94	6	0
271-63	3	11.0	--	4	26	1.8	50	10	91	48	53	24	23
271-62-1	3	11.0	--	4	26	1.8	50	20	84	65	78	16	5
271-62	3	11.0	--	4	26	1.8	50	60	84	79	95	5	0
271-63	3	11.0	--	4	26	1.8	50	60	86	79	92	8	0
271-64	3	11.0	--	4	26	1.8	40	60	89	75	85	12	3
271-66	1	0	(11) $CHCl_3$ (25)	1.5	--	2.0	40	60	85	0	0	0	100[b]
271-69	3	0	CH_3NO_2 (25)	4	--	1.8	50	60	78	--	Mostly DADN[c]		
271-70	3	0	CH_3NO_2	12	--	5.35	50	60	81	65	85	15	0[d]

[a] Multiple of stoichiometric requirement used.

[b] Hetero reaction - DADN insoluble.

[c] Hetero reaction - DADN - not completely soluble.

[d] DADN soluble.

DANNO Process

DANNO (1,5-diacetyl-3-nitro-7-nitroso-1,3,5,7 tetraazacyclooctane), like the preceeding HMX precursors DAPT, TAT, and DADN, is also a known compound (fig. 6). The use of dinitrogen tetroxide in the cleavage of bicyclononane derivatives like DAPT was described by Aristoff and co-workers (ref. 18). These investigators employed a large excess of 98% nitric acid and dinitrogen tetroxide to convert DAPT to DANNO in yields of 75%. Thyagarajan (ref. 25) found that treatment of DAPT with fuming nitric acid afforded a 76% yield of DANNO. Further, it was noted that DANNO was readily oxidized to DADN by treatment with absolute nitric acid. These observations led us to believe that the formation of DANNO may have advantages over the DADN process since the use of sulfuric acid would be eliminated, reducing the number of acids in the overall process to three (acetic, phosphoric, and nitric).

DANNO Synthesis

The preliminary efforts to prepare DANNO from DAPT are shown in table 19. Solid DAPT was added to mixtures of red fuming nitric acid and absolute HNO_3 at temperatures ranging from 0°C to +10°C. The time of reaction was also varied. Various additives were added in an effort to convert the product directly to DADN without isolating DANNO and to determine whether the presence of water and acetic acid has any detrimental effects.

It is quite evident that the presence of N_2O_4 is necessary to produce DANNO, since no product was obtained using absolute nitric acid. Comparison of runs 3 and 4 with 8 indicates that longer reaction times and higher temperatures tend to lower the DANNO yield. In run 6 an effort was made to replace most of the fuming nitric with absolute nitric. It was assumed that red fuming nitric contained 30% N_2O_4. Since the reaction of 2 grams of DAPT requires 1.735 g N_2O_4, 4 ml of red fuming nitric was chosen, since a slight excess of N_2O_4 would be present (1.92 g). Comparison of run 5 with runs 6 and 7 indicates that 4 ml of red fuming nitric is close to the optimum. With regard to the in situ conversion of DANNO to DADN, the addition of urea to remove excess N_2O_4 or PPA or P_2O_5 to remove water did not produce the desired effect. On the other hand, the presence of water and acetic acid had very little effect on the DANNO yield. This observation indicated that a "one-pot" operation similar to the DADN process may be possible.

Table 19. DAPT to DANNO preliminary data

Run no.	Notebook no.	DAPT (g)	RF HNO_3 (ml)	Abs. HNO_3 (ml)	Urea (g)	PPA (g)	P_2O_5 (g)	AcOH (g)	H_2O (g)	Temp (°C)	Add time (min)	Total time (min)	Product	Yield (%)	MP (°C)
1	302-32	2	--	10	--	--	--	--	--	0-10	5	30	--	0	--
2	302-32	2	10	--	--	--	--	--	--	0-10	5	30	DANNO	76.5	225
3	302-32	2	10	--	--	--	--	--	--	0-10	5	60	DANNO	55	225
4	302-32	2	10	--	--	--	--	--	--	0-10	5	30	DANNO	45	223
										20-25	--	15			
5	302-32	2	2	10	--	--	--	--	--	0-10	5	30	DANNO	36	223
6	302-32	2	4	10	--	--	--	--	--	0-10	5	30	DANNO	69	227
7	302-32	2	4	10	--	--	--	--	--	0-14	5	30	DANNO	75	226
8	302-32	2	4	10	--	--	--	--	--	0-10	5	15	DANNO	81	227
9	302-32	2	4	10	1	--	--	--	--	0-10	5	15	DANNO	46	228
										0-10	5	15			
10	302-32	2	10	--	0.7	--	--	--	--	0-10	5	15	DANNO	54	224
										0-14	5	10			
11	302-32	2	4	10	--	6.7	--	--	--	0-10	5	30	DANNO	71	228
12	302-32	2	4	10	--	--	2.2	--	--	0-10	5	15	DANNO	65	228
										0-10	5	15			
13	302-35	2	4	10	--	--	--	0.61	1.1	0-10	10	20	DANNO	66	227
14	302-35	2	4	--	--	--	--	0.61	0.18	0-10	10	20	Very little product		
15	302-37C	2	10	--	--	--	--	--	--	0-10	5	15	DANNO	70.5	--
16	302-37A	2	4	10	--	--	--	--	--	0-10	5	15	DANNO	67.5	228
17	302-32	1 (DANNO)	--	10	--	--	--	--	--	0-10	5	15	DADN	92	268

Experimental work on the development of a one-pot reaction of hexamine to DANNO is given in table 20.

Using the same conditions for DAPT preparation as previously described under the "DADN Process," attempts were made to prepare DANNO via addition of the DAPT-AcOH-H_2O solution to red fuming (RF) nitric acid. Using a weight ratio HNO_3/DAPT solution of 5.65:1.0, a temperature of 0°C and a reaction time of 8 minutes, yields of DANNO in the order of 88% were achieved. All attempts to convert DANNO to DADN in situ were unsuccessful. However, Thyagarajan's observation that DANNO can be converted to DADN in 95% yield using absolute HNO_3 was confirmed. Efforts at this point were concentrated on the conversion of DANNO to HMX via nitrolysis.

HMX Synthesis

Preliminary efforts to prepare HMX by nitrolysis of DANNO are shown in tables 21, 22, and 23. These experiments were conducted to determine the effects of temperature, nitric acid quantity, and addition mode on the conversion of DANNO to HMX. In all of these experiments, the conversion was incomplete. The crude yields ranged as high as 90%; however, on the basis of nmr analysis, the product contained only 20 to 60% HMX, with the remainder being SEX (trinitroacetyltetraacyclooctane) and DADN.

Temperature staging experiments were more successful. In these experiments, DANNO was added to 15 grams of nitric acid at 8 to 10°C, and this temperature was maintained for 15 minutes. During this period, based on data obtained for the oxidation of DANNO, DANNO is converted in 95% yield to DADN. The PPA was then added and the temperature raised to 55° and maintained for 60 minutes. This comprises the first stage. At this point, additional nitric acid or nitric/PPA was added and temperature maintained at 55° for 30 minutes. In the third stage, the temperature was raised to 65° and held 30 minutes. Under these conditions (302-60B in table 24) a crude yield of 79% was obtained,which was comprised of 92% HMX. On this basis the yield of HMX was 73%, the highest attained during these experiments.

Table 20. Hexamine to DANNO via DAPT solution[a]

Notebook no.	DAPT soln. (g)	RF HNO_3 vol x 1.6 (g)	Wt ratio HNO_3-DAPT	Temp (°C)	Add time (min)	Total time (min)	DANNO (g)	DANNO yield[b] (%)	
302-46	17.7	64	3.62	-20	5	15	3.18	34.8	T=constant
302-46A	17.7	96	5.42	-10	5	15	4.50	49.3	T=constant
302-46B	16.5	160	9.7	-20	5	15	5.50	64.6	T=constant
302-47	17.0	64	3.76	0	5	15	5.92	66.8	T=constant
302-47A	17.0	96	5.65	0	5	15	6.28	73.6	T=constant
302-47B	17.0	160	9.43	0	5	15	5.60	63.2	T=constant
302-48	17.0	64	3.76	10	5	15	4.80	55.0	T as low as 0°C as high as 14°C
302-48A	17.0	96	5.65	10	5	15	5.15	59.0	T as low as 5°C as high as 20°C
302-48B	17.0	160	9.43	10	5	15	3.79	43.5	T=constant
302-49	17.0	96	5.65	0	4	8	7.50	85.7	T=constant
302-49A[c]	17.0	96	5.65	0	4	8	7.66	87.6	T=constant
302-49B	17.0	96	5.65	0	2	3-4	7.45	85.1	T=constant
302-51	53.8	288	5.35	-5 +3	4	8	23.0	84.0	T=constant
302-51A	53.8	288	5.35	0	3	8	24.1	87.8	T=constant

[a] DAPT solution: 14 g hexamine (0.1 mole)
6.2 g NH_4OAc (0.08 mole)
7 ml H_2O (0.39 mole)
26.5 g Ac_2O (0.26 mole)

[b] Based on hexamine, 14 g.

[c] Fresh unopened RF HNO_3; all others with previously opened bottle.

Table 21. Effect of temperature on crude yield, DANNO nitrolysis

Notebook no.	Temp (°C)	Time (min)	DANNO (g)	HNO_3 (g)	PPA* (g)	Yield (%) DANNO basis	Composition (5) HMX	SEX	DADN
302-55C	50	90	6	15	54	89.5	23	47	30
302-55D	50	120	6	15	55	89.0	20	43	37
302-56D	55	90	6	15	56	87.5	41	33	25
302-57	60	90	6	15	54	80.5	44	33	23
302-57A	65	90	6	15	54	67.7	63	24	10
302-58	70	15	6	15	54	74.0	26	52	22

*Wt % PPA = 78-79.

Table 22. Effect of nitric acid on crude yield

Notebook no.	HNO_3 (g)	Temp (°C)	Time (min)	DANNO (g)	PPA* (g)	Crude yield (%) DANNO basis	Composition (%) HMX	SEX	DADN
302-56D	15	55	90	6	56	87.5	41	33	25
302-57B	22	55	90	6	82	87.0	34	39	27
302-58C	30	55	90	6	112	84.0	40	37	23
302-57	15	60	90	6	54	80.5	44	33	23
302-57D	22	60	90	6	82	76.6	59	23	18
302-58	15	70	15	6	54	74.0	26	52	22
302-58A	22	70	15	6	82	75.0	23	45	33

*Wt % PPa = constant at 78-79.

Table 23. Mode of addition effects

Notebook no.	Mode of addition	Temp (°C)	Time (min)	DANNO (g)	HNO_3 (g)	PPA (g)	Yield (%) DANNO basis	Composition (%) HMX	SEX	DADN
302-56D	Low temp DANNO-HNO_3 Reaction: PPA added cold Temperature then raised.	55	90	6	15	56	87.5	41	33	25
302-57E	Low temp DANNO-HNO_3 Reaction: DANNO-HNO_3 Solution added to PPA at 55°	55	90	6	15	56	74.0	45	33	22

Table 24. Temperature staging experiments*

Notebook no.	Stage 1 Temp (°C)	Stage 1 Time (min)	Stage 1 HNO_3 (g)	Stage 1 PPA (g)	Stage 2 HNO_3 (g)	Stage 2 PPA (g)	Stage 2 Add temp (°C)	Stage 2 React temp (°C)	Stage 2 React time (min)	Stage 3 Temp (°C)	Stage 3 Time (min)	Crude yield (%) DANNO basis	Composition (%) HMX	SEX	DADN	ATX
302-58D	10	20	15	0	15	112	10	55	90	--	--	80.0	50.0	26.0	24.0	0
302-59B	55	30	15	56	15	56	55	55	60	--	--	83.0	44.5	33.2	22.3	0
302-59C	55	30	15	56	15	56	55	--	--	60	60	74.7	77.6	14.6	7.8	0
302-59D	55	60	15	56	15	56	55	--	--	60	60	82.5	65.3	28.8	5.9	0
302-60	55	60	15	56	15	0	55	--	--	60	60	77.0	85.7	13.0	1.3	0
302-60B	55	60	15	56	15	0	55	55	30	65	30	79.3	91.9	8.1	0	0
302-60C	55	60	15	56	22.5	0	55	55	30	65	30	77.3	90.0	5.0	0	5

*DANNO = 6 grams.

Comparison of the DADN and DANNO Processes

The similarity of the two processes is shown in the following scheme:

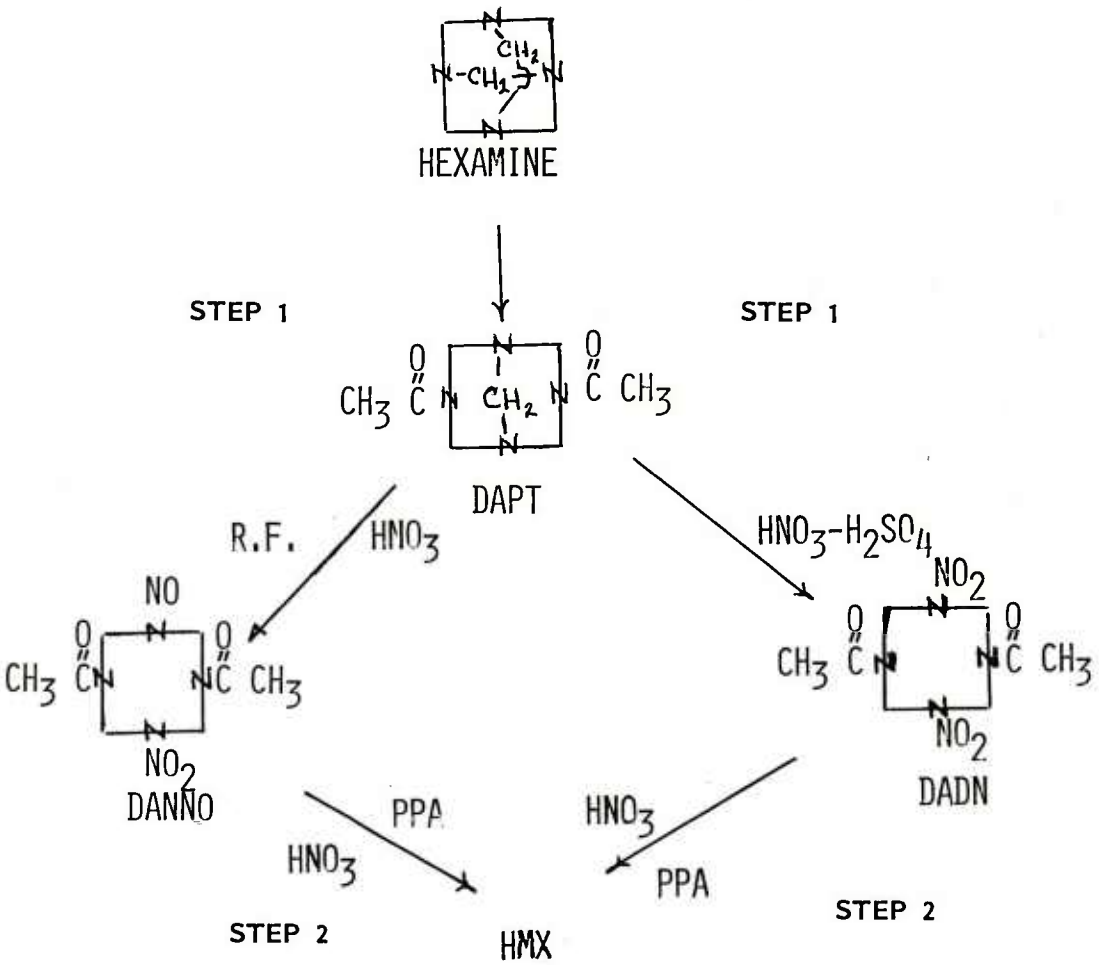


Figure 6. HMX via DANNO and DADN processes.

The major advantage that the DANNO process offers is that the requirement for sulfuric acid can be eliminated. Further comparison with the DADN process is shown in table 25.

Table 25. Comparison of DANNO and DADN process

	DANNO	DADN
Yield, step 1 (%)	88	95
Yield, step 2 (%)	73	82
Yield, overall (%)	64	78
Time, step 1 (min)	18	25
Time, step 2 (min)	110	45
Time, overall (min)	128	45
Quench ratio (wt basis)	3:1	1:1

The DANNO process gives lower HMX yields and requires longer time and excessive water for isolation. These disadvantages offset the advantage of sulfuric acid elimination. The decision was therefore made to carry out the advanced development on the DADN process. This work is covered in the following section of this report.

ADVANCED DEVELOPMENT - THE DADN PROCESS

The DADN process was selected as the process for scale-up, optimization, and laboratory pilot-plant studies based upon high HMX yields and the ease with which it can be prepared. The Advanced Development studies were conducted in two parts. The first part was a joint effort of the Los Alamos Scientific Laboratory (LASL) and the Energetic Materials Division of ARRADCOM using conventional chemical and engineering techniques. LASL was responsible for optimization and piloting studies carried out as the first step of the overall process (specifically, the preparation of DADN from hexamine), while ARRADCOM conducted studies related to the development of the nitrolysis step (DADN to HMX) and acid recovery and recycle. The second part of the study was conducted by the Chemical Systems Division of United Technologies Corporation (UTC) under the sponsorship and management of the Project Manager for Plant

Base Modernization, Contract DAAA21-75-C-0251. In this phase, the overall process was carried out in three steps (hexamine to DAPT, DAPT to DADN, and DADN to HMX), using the inert carrier process (ICP).

Process Development Studies on DADN at LASL

The studies made at LASL are summarized in three reports (refs. 40, 41, 42) and a patent (ref. 43).

In the initial work (ref. 40), the stoichiometry for the DAPT synthesis was optimized, with a reduction in reagent quantities over those required for the original ARRADCOM procedure. Engineering studies of the DAPT process covered modes of addition and mixing, reaction temperature, cooling requirements, and rates of reaction. The feasibility of a continuous process for DAPT manufacture was demonstrated. A study was also made of the mechanism of the nitrolyis of DAPT to DADN. The abrupt exotherm occurring during this step was found to be caused by the oxidation of formaldehyde by nitric acid, a reaction catalyzed by both water and acetic acid. The exotherm can be eliminated by the addition of urea (ref. 43), which presumably forms an adduct with formaldehyde, which is stable to nitric acid oxidation. Elimination of the exotherm permitted a safe increase in the reaction temperature, with a consequent drastic reduction in reaction time without reduction in yield or product purity. It was concluded that a continuous process for preparing DADN using near-stoichiometric amounts of nitric acid might be feasible.

A continuous pilot study was made (ref. 42), yielding 13.6 lb DADN/hour, with a feed rate of 7 lb hexamine hour. A conversion of 0.94 moles DADN/mole hexamine was obtained and product purity was 98%; these results were about the same as those obtained in the laboratory. The most important finding in this study was the influence of the quenching method on process yield. Although all runs were to have been conducted with a continuous quench, a pump failure forced a number of runs to be made with a semi-batch quench; the conversions in these runs were all relatively low. Later runs, made with a replacement pump, gave conversions comparable to the laboratory work. The low conversions in the semi-batch quenches were not related to the nitrolysis step, but were the result of destruction of DADN in quenching. The relatively slow dispersion and solution of the reaction mixture in the quench water restricted the dissipation of the heat of dilution and allowed destructive temperatures

to be reached at the point of mixing. In contrast, the Venturi mixer (eductor) used in the continuous quench allowed rapid intimate mixing of the two streams and a very small temperature rise occurred. In all other respects, the plant operated as planned, producing DADN at the desired rate, conversion, and purity. Equipment, raw material, utility, and labor requirements are projected on the basis of these data for a plant producing 500,000 lb DADN per month at 85% of full-time capacity.

Optimization of Nitrolysis

DADN can be nitrolized to HMX by using a variety of nitrating reagents. Of these reagents, N_2O_5 is the obvious choice to be used in the DADN process due to the fact that the by-products of the nitrolysis reaction would be acetic acid and nitric acid, thereby simplifying the separation and recovery aspects of the process. Unfortunately, there is no practical industrial method for preparing N_2O_5 at present. Of the remaining reagents, polyphosphoric acid was considered to be the next most practical due to its lower cost and the fact that industrial methods are available to recycle ortho-phosphoric acid to a superphosphoric acid of 76% P_2O_5 content. Although polyphosphoric acid has a P_2O_5 content of approximately 83%, it may be possible to concentrate O-H_3PO_4 further to achieve this level. It was decided, therefore, to optimize the nitrolysis of DADN using the PPA/HNO_3 reagent.

In our early work on the PPA-HNO_3 system, we established that large quantities of nitric acid and long reaction times are required to produce HMX in reasonable yields. The object of the optimization effort was, therefore, to reduce the quantity of nitric acid required and to obtain high yields of HMX within a time period of 15 to 30 minutes. Using the weight ratio 1:3.73 of nitric acid to PPA (80 wt % PPA) established earlier as near the optimum for efficient conversion of DADN to HMX and arbitrarily choosing a DADN to HNO_3 ratio of 1:2.5, the course of nitrolysis as a function of temperature was observed for 90-minute reaction times. The data obtained, shown graphically in figure 7, indicate that DADN is nitrolized to HMX through the intermediate trinitroacetotetraazacyclooctane (SEX) and that a minimum temperature of 65°C is required under these conditions to produce a 72.8% yield of HMX having a purity of approximately 97%. The nitrolysis reactions were then conducted at 65°C for 90 minutes using the 1:9.33 DADN to PPA ratio established by the first set of conditions in an attempt to find the minimum concentration of nitric acid necessary to achieve the same yield shown in figure 7.

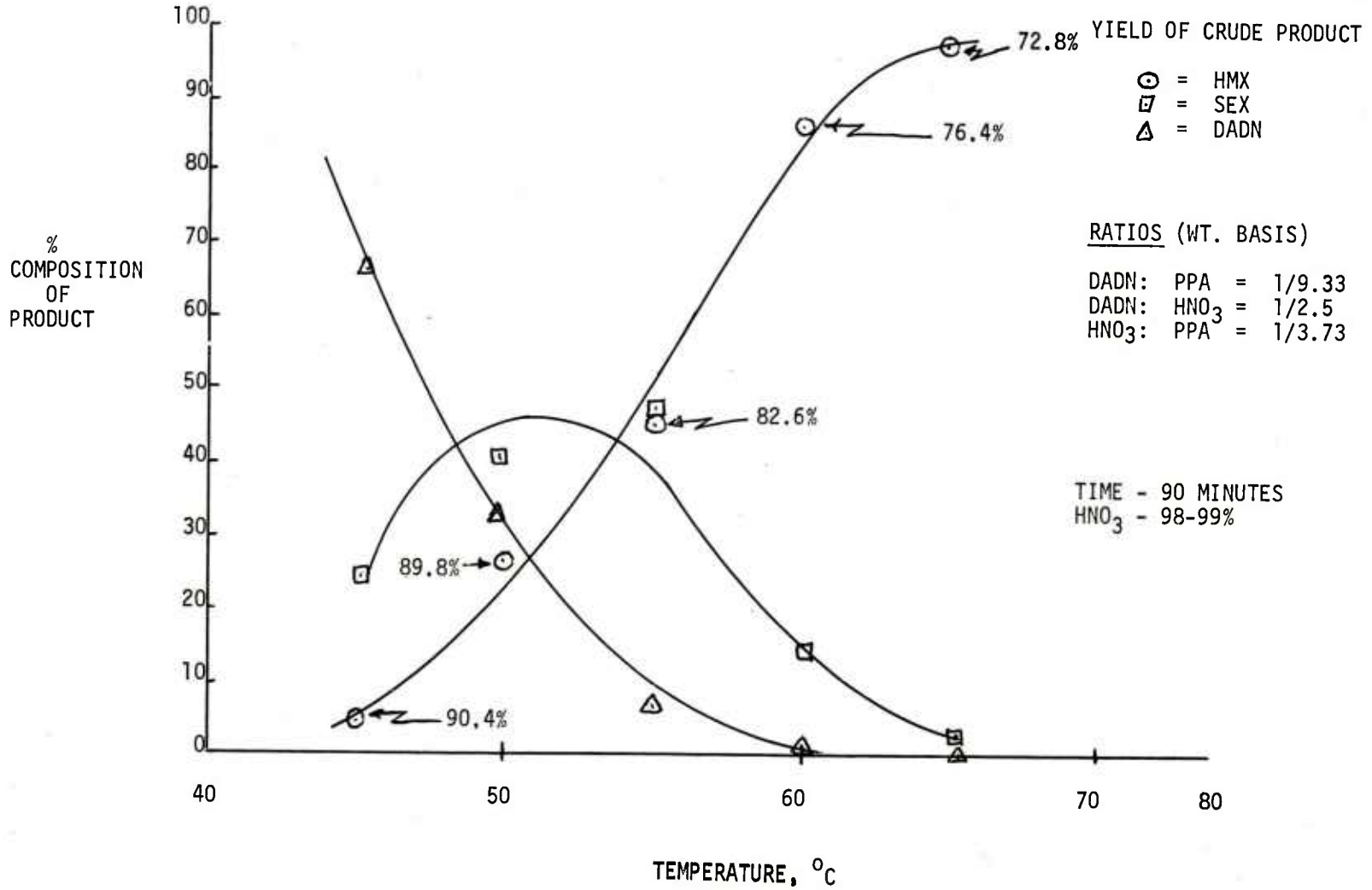


Figure 7. DADN nitrolysis: yield vs temperature.

As shown in figure 8, a weight ratio of nitric acid to DADN of 3.67:1 was necessary to achieve complete nitrolysis and a yield of 74.4%. At lower HNO_3:DADN ratios, the conversion was incomplete and the HMX purities ranged from 60 to 97%. The same experiments were performed at 70°C and 75°C for 30 minutes. At 70°C (fig. 9), it appears that 30 minutes is not quite enough to complete the reaction at the 3.6:1 HNO_3:DADN ratio, since the purity of HMX is only about 85%. In this case, the ratio of HNO_3 to DADN had to be increased to 5:1. At 75°C, however, (fig. 10), 30 minutes is ample time for complete conversion and the ratio of HNO_3:DADN was again found to be 3.67:1. Under these conditions, a 76% yield of 100% pure HMX is attainable. Two experiments were also conducted at 80°C; however, no apparent advantage over 75°C was observed as a reaction time of approximately 30 minutes was required to produce HMX in the same yield as found at 75°C (fig. 11). At 80°C, some linear nitramines were found in the product, indicating that degradation was occurring. Having established that the near optimum HNO_3:DADN ratio is 3.67:1, the optimum ratios on a weight basis become HNO_3:DADN 3.67:1, HNO_3:PPA 1:2.55 or (71 wt % PPA), and DADN:PPA 1:9.33.

Several experiments were performed in an attempt to evaluate the effects of nitric acid strength and of nitric acid-polyphosphoric acid preheating on HMX yields. It was found that nitric acid strength is critical to the success of the nitrolysis. Increased yields of approximately 5% can be realized when 100% HNO_3 is used as opposed to 98-99% HNO_3. This is shown clearly in figure 11. For example, the HMX yield in the nitrolysis experiments at 65°C for 90 minutes was 74.4% using 98-99% nitric acid as opposed to 80.3% with 100% HNO_3. The yield of HMX was also increased to 80% at 75°C for 30 minutes and at 70°C for 60 minutes, when 100% HNO_3 was used. The same effect was observed when 98-99% HNO_3 was preheated with PPA at 65°C for 15 minutes prior to DADN addition.

The major findings from this program thus far are as follows:

1. The maximum yield of HMX attainable in the DADN nitrolysis step is in the order of 80 to 81% of the theoretical.

2. The optimum temperature-time parameter appears to be 75°C for 20 to 30 minutes. Temperatures below this require excessive time and those above lead to degradation indicated by an increase in linear nitramines.

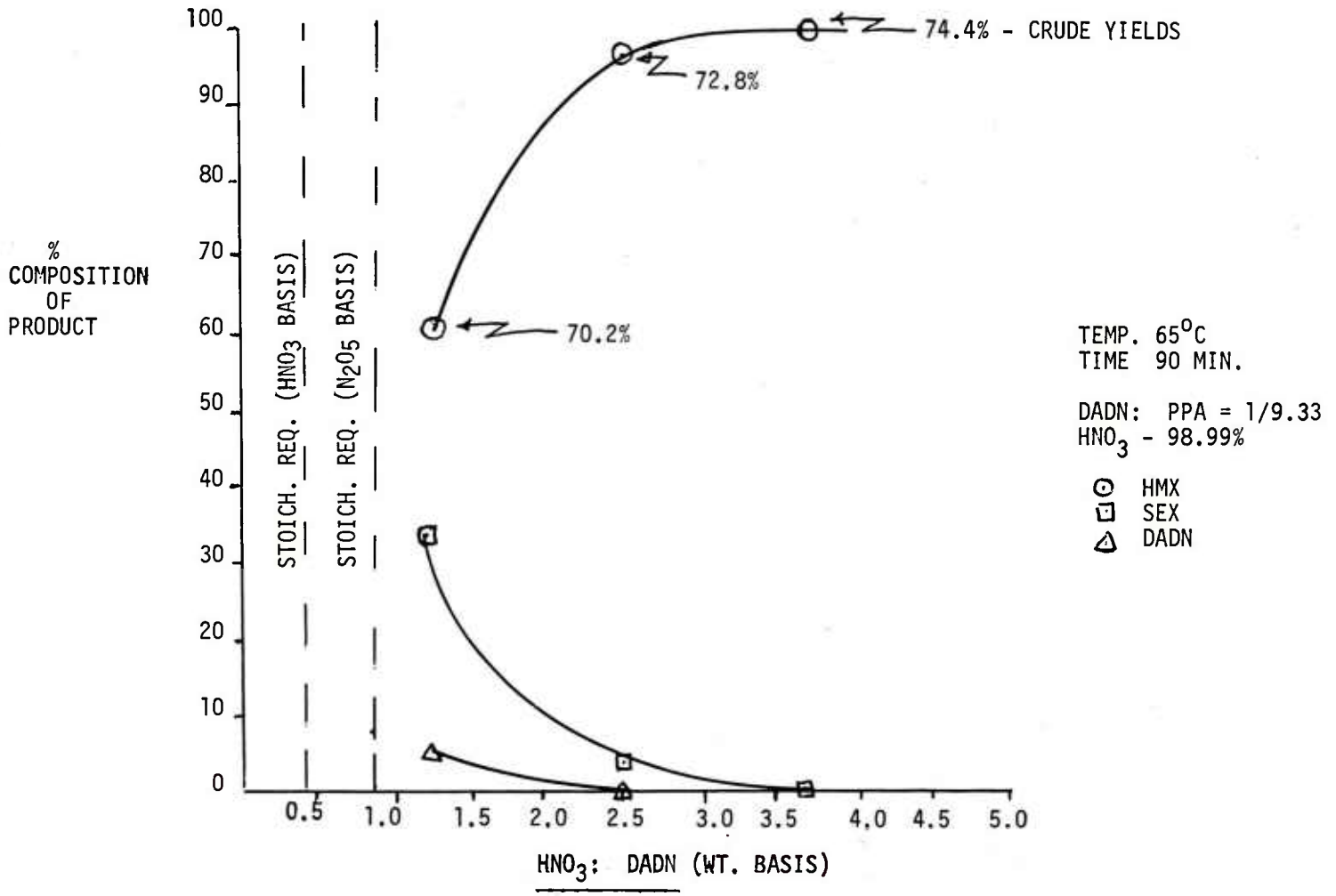


Figure 8. DADN nitrolysis: yield vs nitric acid usage (65°-90 min).

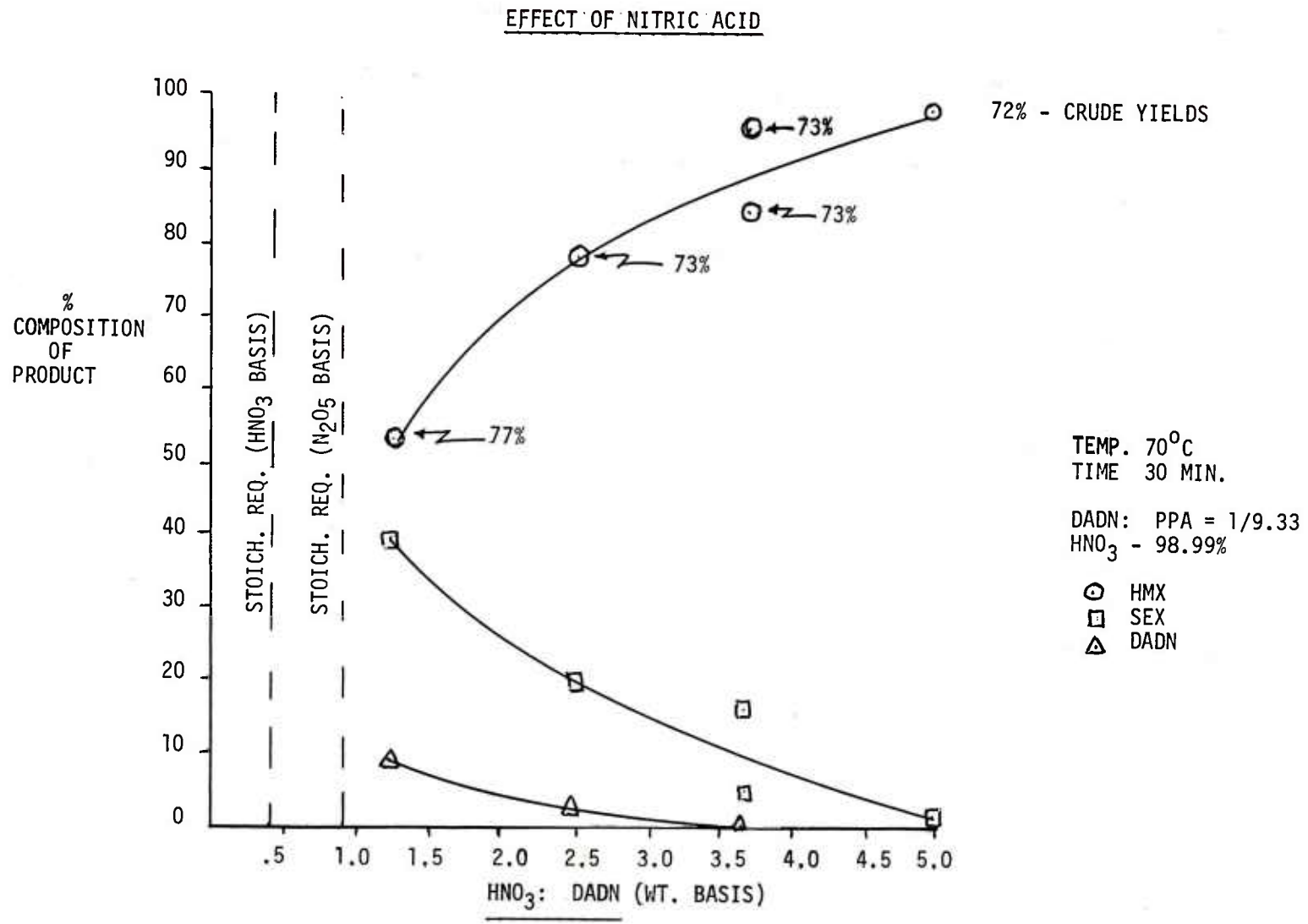


Figure 9. DADN nitrolysis: yield vs nitric acid usage (70°-30 min).

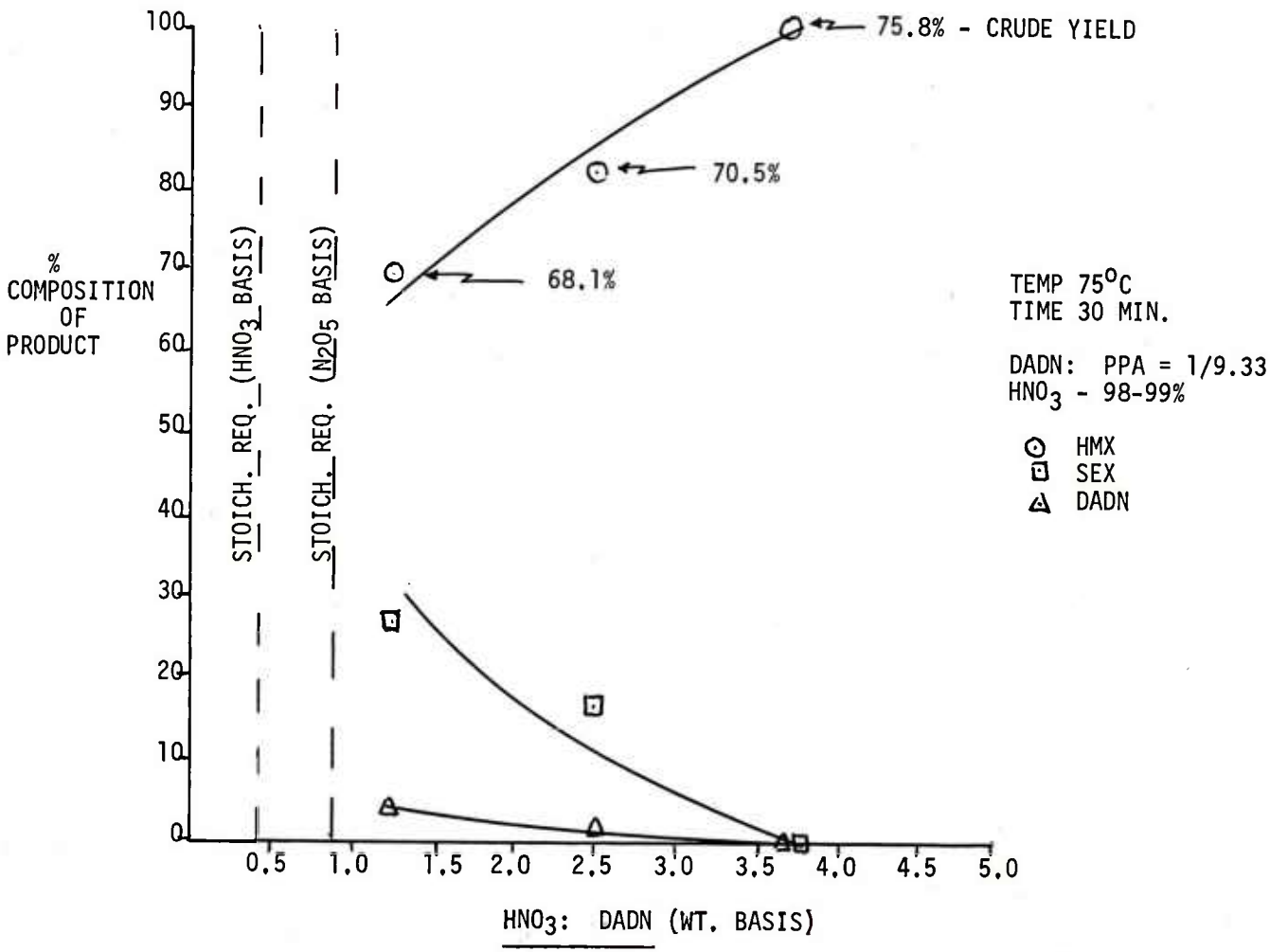


Figure 10. DADN nitrolysis: yield vs nitric acid usage (75°-30 min).

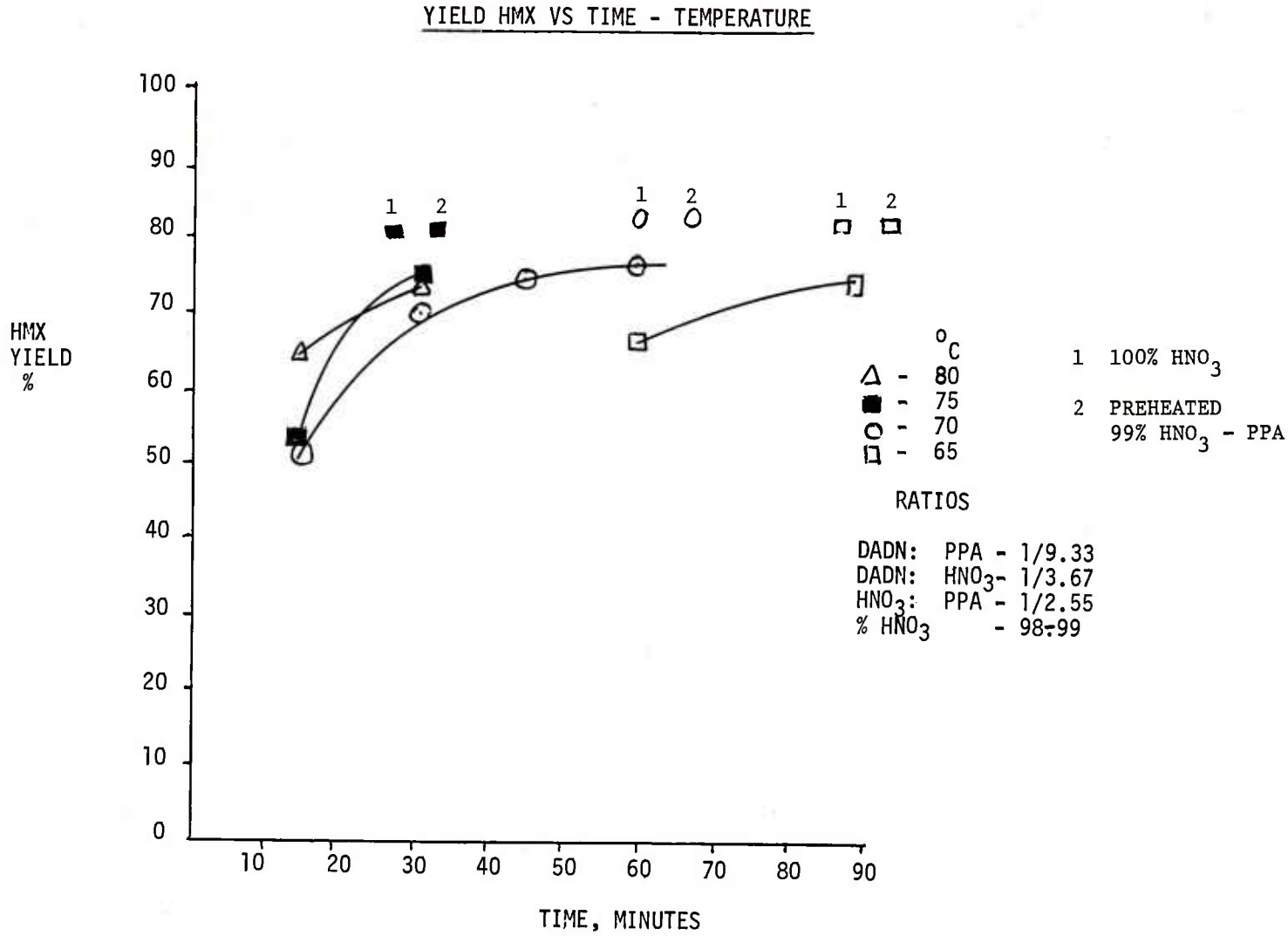


Figure 11. DADN nitrolysis: yields vs time, temperature, nitric acid strength.

3. The optimum reactant ratios determined thus far are (on a weight basis) HNO_3/DADN = 3.67/1; HNO_3 PPA = 1/2.55; and DADN/PPA = 1/9.33. Further work, however, is required to determine whether the PPA requirement can be reduced.

4. The maximum HMX yields are achieved through the use of 100% HNO_3. Use of 98% nitric acid results in yeild reductions of 4 to 5%. This reduction can be overcome, however, if preheated 98% HNO_3 PPA mixtures are employed.

5. Rapid agitation practically eliminates the excessive foaming previously encountered.

Acid Recovery

Several scale-up experiments were performed to demonstrate the feasibility of acid recovery. In these experiments, the optimum conditions previously determined were not carefully controlled. The main emphasis was on acid recovery. Table 26 shows, however, that at ratios close to the optimum, yields of fairly pure HMX in the order of 78% were obtained. At the end of the reaction period, prior to quenching, the HNO_3 was recovered by distillation at 20 mm of Hg Titration with 0.1 N NaOH gave HNO_3 values of 103.5 to 118% recovery. These high values are due to the presence of nitrogen oxides which are converted to nitric acid upon dilution with water prior to titration. After cooling to 15°C, the remaining mixture was quenched on ice and the HMX filtered off. The filtrate was distilled at 20 mm of Hg to remove the acetic acid leaving O-phosphoric acid in the distilling flask. Titration of these fractions with 0.1 N NaOH gave recovery values ranging from 61 to 79% for acetic acid and 97 to 104% for phosphoric acid.

These preliminary experiments demonstrate that acid separation and recovery in the DADN process is feasible and that no apparent difficulties exist.

Polyphosphoric Acid Regeneration

The key to the successful conduct of the DADN process is the regeneration of polyphosphoric acid (PPA) from the ortho-phosphoric acid produced during the isolation of HMX. Industrial methods, using concentration technologies are geared to the manufacture of superphosphoric acid of 76% P_2O_5 content. In order to perform the nitrolysis step, this

Table 26. DADN nitrolysis - scale-up

HNO_3:DADN (wt basis)	PPA-DADN ratio (wt)	HNO_3:PPA ratio (wt)	Reaction temp (°C)	Reaction time (min)	Crude HMX yield (%)	Purity (%)	HMX yield (%)	Acid HNO_3	Recovery (%) AcOH	Recovery (%) H_3PO_4
7.8/1	17.41[a]	1/2.22	70	15						
			65	15	90.9	92.1	83.7	118.0	61.0	104.0
			60	30						
7.66/1	17.7/1	1/2/31	70	15						
			65	15	91.4	90.8	84.0	103.5	68.6	97.4
			60	30						
3.75/1	8.3/1[b]	1/2.22	70	10						
			65	50	81.0	96.6	78.2	109.81	78.7	97.1
3.8/1	8.44/1[b]	1/2.22	70	5						
			65	25	80.3	95.7	76.8	105.7	77.6	98.3
			60	30						

[a] 15 grams DADN.

[b] 30 grams DADN.

level must be raised to the 83 to 85% P_2O_5 or 117% H_3PO_4 level present in commercial PPA. The problem, therefore, was to find the conditions necessary to achieve the higher P_2O_5 level and to determine whether nitrolysis can successfully be carried out using PPA regenerated under these conditions.

Table 27 shows the results of experiments starting with 85% phosphoric acid. In these experiments, the vacuum distillations were carried out in all-glass apparatus. The glass was attacked at the elevated temperatures used and resulted in a PPA containing some solid silicates which could not be removed by filtration. The % H_3PO_4 determinations established by titration are, therefore, considered to be erroneous. A truer indication of the nature of the PPA produced was provided by a comparison of the nitrolysis step, using the regenerated PPA, with the results obtained with commercial PPA. The data indicate that yields of HMX comparable to the yields obtained from commercial PPA are attainable at 250°C and 4 mm of Hg for 4 hours and also at 290°C and 20 mm for 4 hours. Even higher yields, on the order of 80%,can be achieved if the evaporation of O-H_3PO_4 is carried out at 290°C and 4 mm Hg for 4 hours.

PPA suitable for the nitrolysis step can be prepared by concentration of O-H_3PO_4. Further work is, however, necessary to determine if it is feasible on a commercial scale.

Optimum Nitrolysis Process

The DADN nitrolysis conditions are summarized in table 28. As indicated, the yield of HMX is 80 to 82% of the theoretical based on the quantity of DADN used. Considering that DADN can be prepared from hexamine in 95% yield (based on hexamine), the overall yield for the entire process is approximately 78% based on hexamine. This yield is considerably higher (about +13%) than that attained by the current process as conducted at Holston AAP. In addition, the quantity of acetic anhydride required in the DADN process is significantly lower than the HAAP process.

The data also indicate that spent acids can be recovered with reasonable efficiency. Preliminary experiments show that orthophosphoric acid can be converted into PPA having properties suitable for recycle into the nitrolysis process.

Table 27. Polyphosphoric acid recycle

Distillation conditions temp (°C)	time (hr)	vacuum (mm)	H_3PO_4 conc (%)	Crude HMX yield (%)	Melting point (°C)	Product composition (%) DADN	SEX	HMX	ATX	HMX yield (%)	HNO_3 strength (%)
250	4	20	107.1	59.4	271	0	4.9	88.2	6.3	52.4	99+
290	1/2	20	108.8	70.7	275	0	1.3	98.7	0	69.5	99+
290	4	20	109.0	74.3	275	0	0.6	99.4	0	73.8	99+
250	2	4	110.0	71.0	275	0	1.2	94.5	4.5	67.1	99+
250	4	4	110.7	74.6	276	0	1.3	96.3	2.4	71.8	99+
290	4	4	109.0	82.7	276	0	0	96.8	3.2	80.0	99+
Commercial PPA			117.7	74.4	278	0	TR	100	0	74.4	99+

Nitrolysis conditions
Temp - 65°C
Time - 80 min
DADN - 6 g

Ratios (wt basis)
DADN/PPA = 1/9.33
DADN/HNO_3 = 1/3.67
HNO_3 = 1/2.55

Table 28. DADN nitrolysis parameters

Temperature (°C)	75
Time (min)	30
Nitric/DADN (wt basis)	3.7:1
PPA/DADN (wt basis)	9.3:1
PPA/HNO_3 (wt basis)	2.6:1
Yield (%)	80-82
Acid recovery (%)	
HNO_3	100
H_3PO_4	98
AcOH	80
PPA regeneration	Yes

Cost Estimate for the DADN Process

The cost analysis in appendix B is based on data generated during exploratory development and part of the advanced development phase of the DADN process.

United Technologies Process Development Studies

United Technologies Corporation (UTC) applied their inert carrier process (ICP) to the new HMX chemistry discovered at ARRADCOM and the University of Idaho, and developed jointly at ARRADCOM and Los Alamos Scientific Laboratory. The work was done by UTC's Chemical Systems Division (CSD) at Sunnyvale, California, and was supervised by the Contact Project Officer, Mr. Thomas Caggiano, AMCPM-PBM-EE. The study covered nine months and was concluded in February 1976. The essential features of the process and a summary of the results obtained, taken from the CSD final report (ref. 44), are shown in figures 12-15 and tables 29-32.

Background

It should be noted that CSD performed some work prior to award of the contract under company-funded independent R&D. Based on this effort, two conclusions were drawn. The first is described in Dr. Colin Hudson's (ARMCOM) trip report dated 21 June 1974, as follows: "Most notably the process (ICP) works at ratios of 1: 2.2: 4 (DAPT: HNO_3 : H_2SO_4) moles of inputs. This is a spectacular improvement over the prior requirement of 3.3 moles of nitric acid and 22: 6 moles of sulfuric acid."

The second conclusion was related to Mr. Siele via a telephone call from Dr. J. F. Schimscheimer of CSD on 24 October 1974. A procedure was described for the conversion of DADN to HMX, using the inert carrier process, which gave an 85% yield of HMX in only 20 minutes. Details are as follows:

Six grams DADN (99% pure) was suspended in 300 ml CCl_4 preheated to 50°C in a 1-liter Teflon beaker. After about 30 seconds, a mixture of 22 grams absolute nitric acid and 50 grams PPA (cooled to 10°C) was added to the suspension with rapid stirring; stirring was continued for 20 minutes at 62-3°C. The mixture was cooled to 40°C mixed with water, and filtered. The product weighed 5.8 grams (94.6% yield) and

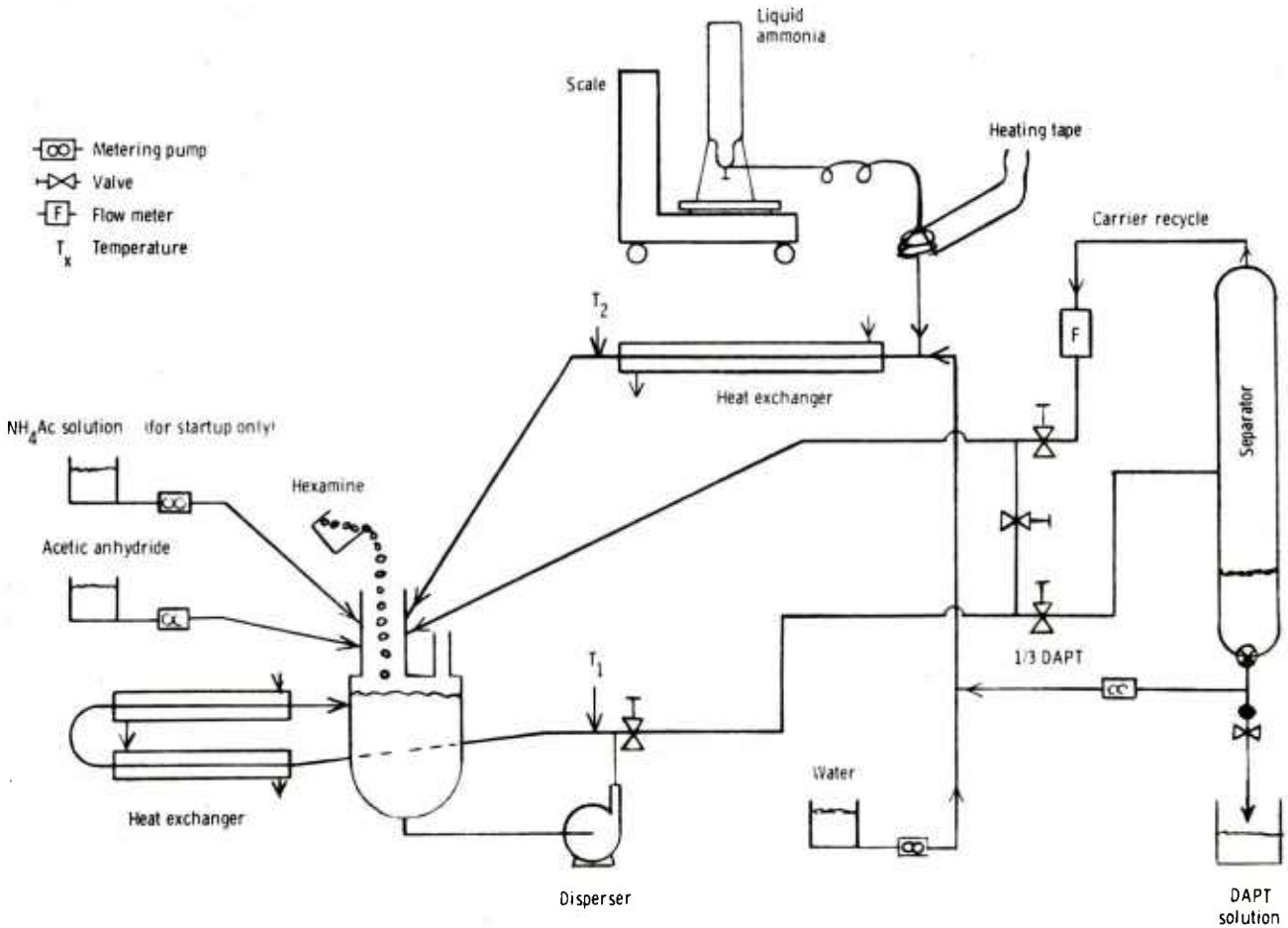


Figure 12. ICP for DAPT manufacture with ammonia addition (single disperser) .

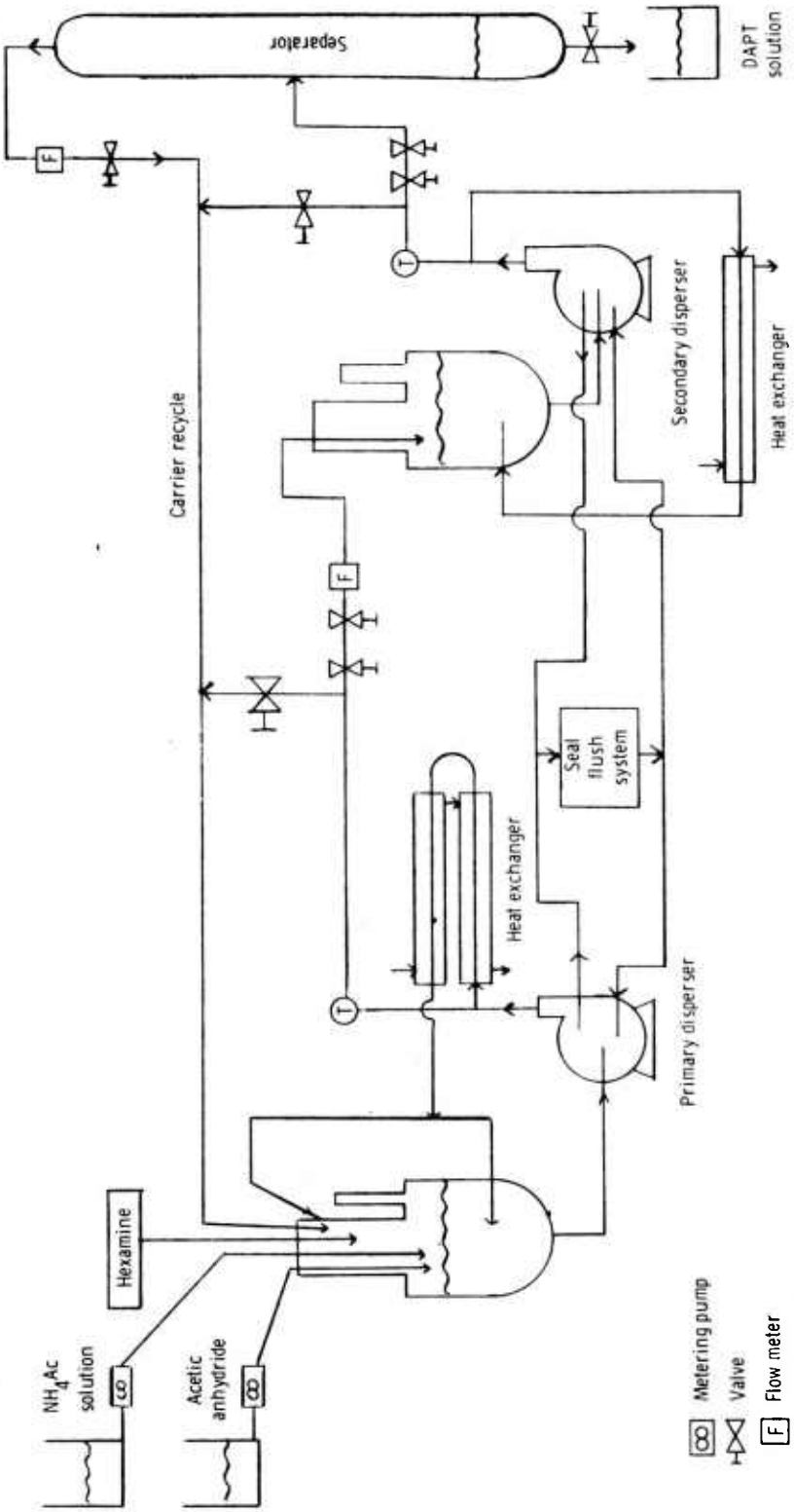


Figure 13. ICP for DAPT manufacture (double disperser).

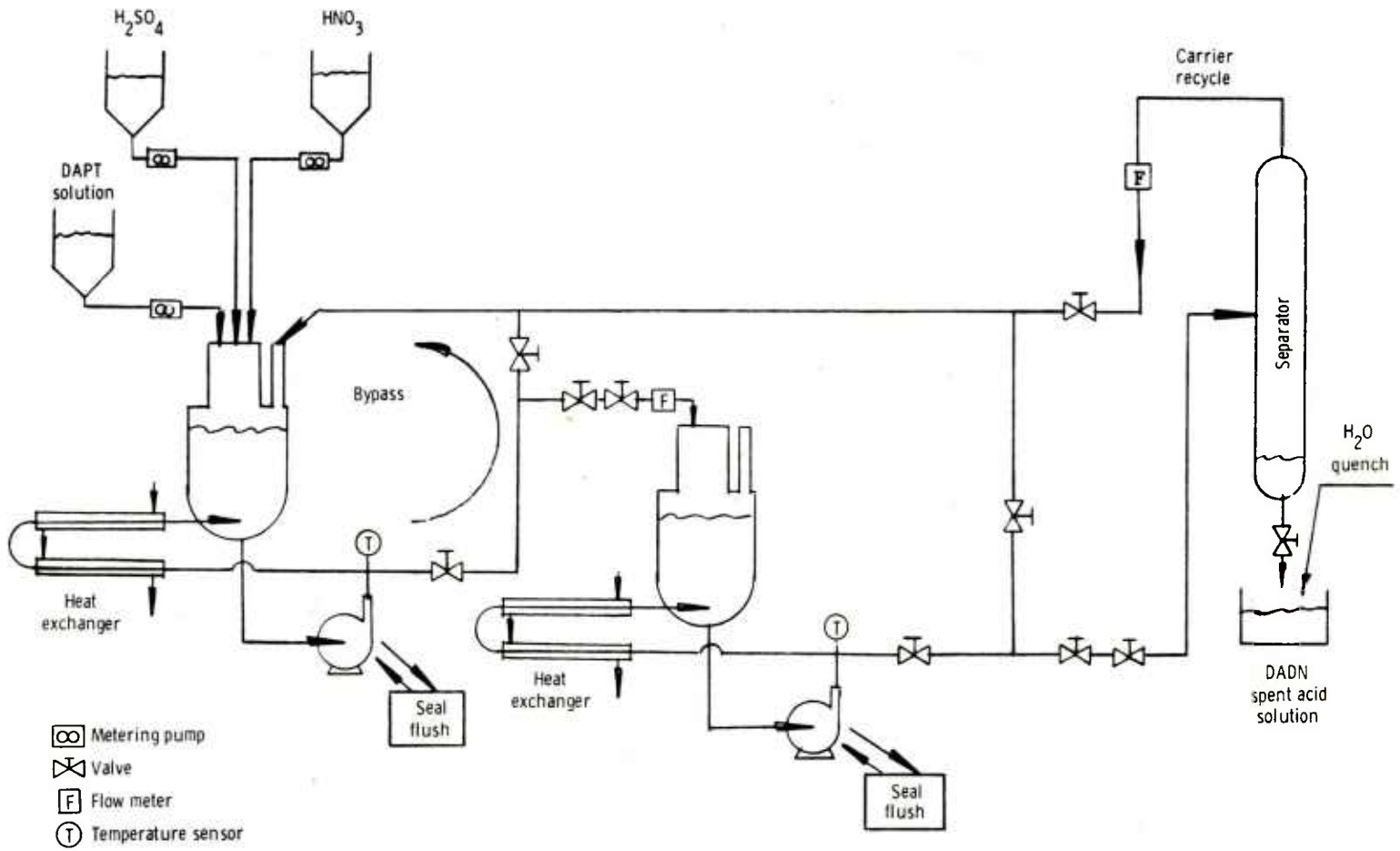


Figure 14. ICP for DADN manufacture (double disperser).

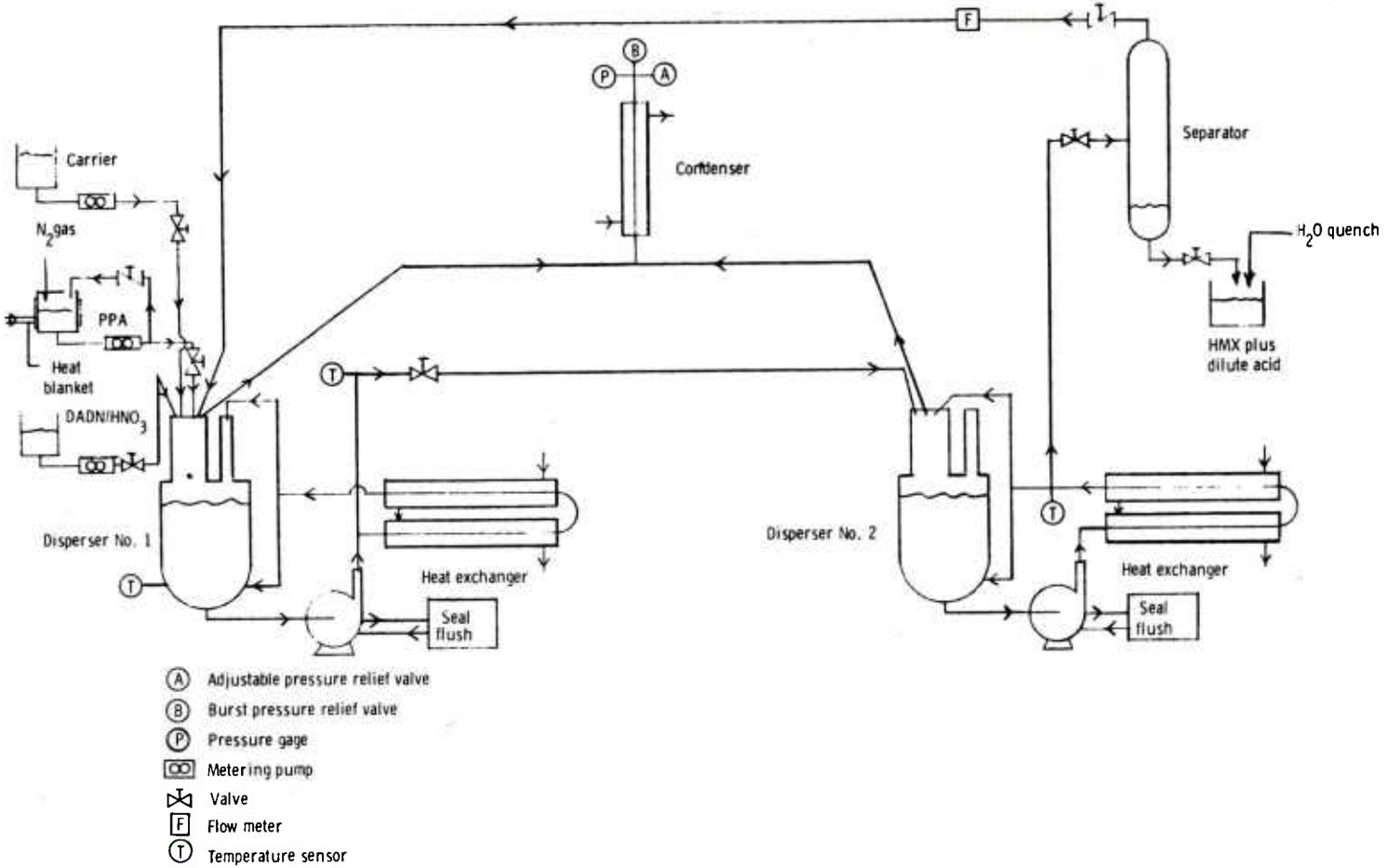


Figure 15. ICP for HMX manufacture (double disperser).

Table 29. Step 1 - hexamine to DAPT

Operating Mode	Time, min	Material Feed Rates, moles/min: Hexamine	Ac_2O	NH_4Ac	NH_3	H_2O	Yield, %	DAPT Solution, lb/hr	DAPT Pure, lb/hr
				Run No. 11					
Single disperser	0 to 8	1.00	2.54	0.77	–	3.99	94	70	27
	8 to 40	1.00	2.54	–	0.87	5.25	–	–	–
				Run No. 13					
Double disperser	78	1.50	3.76	1.21	–	6.32	109	110	45
		(1.00)*	(2.51)	(0.81)	–	(4.21)	–	–	–

*( ) Ratio only

Table 30. Step 2 - DAPT to DADN run no. P-10

Mode	Operating Time, min	Operating Temperature, °C	Mole Ratio DAPT Run 13	Mole Ratio HNO_3 99%	Mole Ratio H_2SO_4 93%	DADN/ Hexamine Yield, %	Purity, %	DADN, lb/hr
Double disperser	160	26	1.00	6.45	22.7	85.5	99	9

Table 31. DADN to HMX run no. P-105

Mode	Operating Time, min	Operating Temperature, °C	Weight, grams DADN	Weight, grams HNO_3	Weight, grams PPA	HMX/DADN Yield, %
Double disperser	108	65/60	3,240 (6)*	11,880 (22)	25,700 (48)	67-1/2

Table 32. DADN-HMX chemistry

CSDs accomplishments:

- DAPT — 200 lb at 45 lb/hr
- DADN — 35 lb at 9 lb/hr
- HMX — 10 lb at 3-1/2 lb/hr

comprised 90% beta HMX and 10% SEX. CSD obtained the same results in a 20-fold scaleup. No foaming was observed. Yields drop off if impure DADN is used, or if a glass reactor is employed. FC-77 (from 3 M, b.p. 98°C) can be used at 80°C instead of CCl_4 to give the same result.

Discussion of CSD Data

For clarity, the following discussion is separated into three parts: step 1, Hexamine to DAPT, step 2, DAPT to DADN, and step 3, DADN to HMX.

Step 1 - Hexamine to DAPT

This step, as performed by CSD using the ICP process, appears to have functioned reasonably well. However, the highest yield obtained was 109% and this yield was the result of only one plant run. In addition, it was obtained with the use of ammonium acetate instead of the more economical ammonia gas. (Ammonia gas is essential to the economic production of DAPT.) When ammonia gas was used, the CSD yields dropped to the 94-99% range. In comparison, Los Alamos, using conventional pilot plant equipment, performed seven plant runs with ammonia and consistently achieved yields of 115%. Lack of the factors claimed to be advantageous to the inert carrier process, such as use of the carrier as a heat sink, reduction of viscosity, etc., has not created any problems in the LASL designed reactor, which does not employ an inert carrier.

In summary, even though CSD has (1) demonstrated that it is feasible to produce DAPT using the inert carrier process, (2) has confirmed original ARRADCOM and LASL data with regard to (a) use of ammonia, (b) degradation of DAPT solutions on storage, and (c) difficulty in DAPT isolation, it has also demonstrated that the ICP technique gives yields of DAPT that are 6 to 20% lower than those obtained by conventional engineering procedures. It is, therefore, considered unnecessary to employ the ICP technique for DAPT production as, based upon CSD data, it clearly gives lower yields than LASL's conventional reactor.

Step 2 - DAPT to DADN

The pilot data presented by CSD indicate that the highest yield of DADN attainable by the ICP technique is 85.5%. This value is based on one run (P-10). A similar run produced DADN at a 5% lower level. CSD has again demonstrated the feasibility of the ICP technique

for the production DADN; however, the CSD yields are 10 to 15% lower than those obtained by LASL in their conventional reactor. CSD confirmed original ARRADCOM-LASL data with respect to the use of 93% sulfuric acid and has confirmed that an oleum plant required for the production of 98% sulfuric acid can be eliminated from the overall manufacturing facility.

More important than the yields, however, is the finding that reduced sulfuric acid levels cannot be used in the formation of DADN. As stated above (see Background), it was earlier thought that such was possible. It is clear from table II, Volume I, of the CSD report and the section on molar ratio: HNO_3/H_2SO_4 (p 20), that sulfuric acid levels below the original ARRADCOM levels cause severe reduction in DADN yields. This confirms original ARRADCOM experiments on the effect of the sulfuric acid level on the DADN yield.

In summary, the ICP process gives a reduced yield of DADN. CSD has confirmed that 93% sulfuric acid can be substituted for 98% sulfuric acid and that reduction in sulfuric acid levels causes severe reduction in DADN yields.

Step 3 - DADN to HMX

During this phase of the program,CSD again demonstrated the feasibility of applying the ICP technique to the third step in the new HMX chemistry, but the yields of pure HMX were considerably lower than ARRADCOM-LASL yields. The highest yield obtained by CSD was on the basis of one run (67.5%) compared to 80% obtained by ARRADCOM on a consistent basis without the carrier.

It is clear from the data compiled by CSD in table IV, Volume I, of their final report that when carbon tetrachloride is used as the inert carrier, regardless of quantity, temperature, or time, the yields of pure HMX are in the order of 9 to 20% as compared to the 85.5% reported earlier (see Background).

Data presented in table IV of the CSD report is reordered below as table 33.

Table 33. HMX yields with inert carriers

Volume (ml)	HMX yield (%)	Temp (°C)	Time (min)	Run no.
FC-48 Carrier				
0	78	65	60	110
47	50	65	60	114
47	58	65	60	122
94	30	65	60	144
94	38	65	60	145
250	26	65	60	137
400	19	65	60	128
FC-77 Carrier				
47	55	65	60	119
160	30	65	60	139

With both of these carriers higher HMX yields are obtained as the carrier level is reduced. Although the data for carbon tetrachloride are not included above, it is evident that the quantity in this case is unimportant since the yields are low (9 to 19%) regardless of amount used. The data presented, therefore, indicate that higher yields of HMX should be attainable with further reduction in carrier and the highest yields should be reached without any carrier. This has been substantiated by CSD in run 110 which employed early ARRADCOM conditions and ratios and no carrier. The yield achieved by CSD was 78% which is very close to the consistent 80% found during experiments at ARRADCOM.

Although CSD has demonstrated that it is feasible to apply the ICP technique to the new HMX chemistry, the yields obtained were consistently lower than those attainable by conventional techniques.

Table 34. ICP process vs conventional ARRADCOM-LASL

Yield	ICP (%)	Conventional (%)
DADN	85.5	95
HMX	67.5	82
Overall	57.7	78.0

CONCLUSIONS AND RECOMMENDATIONS

At the conclusion of this phase of the effort to develop the DADN process, a brief internal report (appendix A) was written by the Manufacturing Technology Division, ARRADCOM. In addition, a decision risk analysis (DRA) was conducted by the Army Armament Materiel Readiness Command at Rock Island, Illinois. In summary, the MTD report concluded that the DADN process offered no advantages over the current improved Bachmann process and, therefore, no further work was planned. The DRA indicated that future HMX production requirements could be met at the lowest cost and risk by Holston Army Ammunition Plant (HAAP) using the Bachmann process.

It is believed that the conclusions set forth in those reports may be premature. First, it is difficult to project what new systems may be developed which may require the additional energy contained in the HMX molecule, i.e., high energy cool-burning gun propellants. One must proceed on the assumption that new systems will be developed by the Army, Navy, and Air Force which may require a substantial HMX production base. If work on alternative HMX processes, including the DADN process, is terminated at this point, the DOD has no choice but to rely on the Bachmann process, which produces HMX at a cost of 5 to 10 times that of RDX, and which, in all likelihood, cannot be improved substantially. In addition, the DADN process can be divided into two phases. In the first, the non-explosive operations can be conducted at sites anywhere in continental North America. The second phase also could be carried out in small plants scattered throughout. This alone offers a logistic advantage over the current Bachmann process operated at HAAP. It is believed that, with minimal expenditure for improvement of the DADN process and development of alternative HMX processes, substantial reduction in HMX costs can be achieved in the future. The following summary of work on the DADN process is submitted with the suggestion that the recommendations be given serious consideration.

1. The study of the three-step DADN process has been conducted at three locations as follows: (1) Energetic Materials Division, ARRADCOM: basic laboratory studies and cost analysis of the entire process; (2) Los Alamos Scientific Laboratory: laboratory and pilot studies of the first two steps; (3) United Technology Center: application of their inert carrier process to all three steps of the process.

2. A cost analysis, made at ARRADCOM late in 1974 by Dr. R. Hutchinson and Mr. R. Motto, showed that the DADN process compared favorably with the Bachmann process, as operated at HAAP, for producing crude HMX. It was pointed out that the DADN process would give cheaper HMX if further improvements were realized. Two of these have since been achieved, the use of 93% sulfuric acid in the second step, and a reduction of reaction time in the third.

3. Pilot studies at Los Alamos have shown that the first step can be operated continuously at a rate of 10 to 15 pounds of product per hour. It is thought that the second step can also be operated continuously.

4. Work at United Technology Center has to date given about 20% lower yields of HMX (60% vs 80%) than in the laboratory at ARRADCOM and at Los Alamos (first two steps). In addition, there have been no indications as yet that the use of an inert carrier is beneficial. It is therefore felt that no further work in this direction should be undertaken.

5. In view of the favorable cost study cited above and the promising results from the pilot studies at Los Alamos, it is recommended that work continue on the DADN process. The third step of the process should be studied on the pilot level, at Los Alamos or elsewhere, comparable to the studies now in progress on the first two steps. This would provide a sound basis for an up-to-date cost study of the entire process in about one year. At the same time, a further laboratory study of the reconcentration of the spent polyphosphoric acid (PPA) from the third step - with special emphasis on commercially practical materials of construction is proposed. This is estimated to require one year. Development of analytical and acid recovery procedures is also required. The entire cost of this MM&T-type program is estimated at $250,000.

6. In addition, we propose a supporting R&D program aimed towards fundamental improvement of the third step, which at present employs a large volume of PPA. This acid must be reconcentrated for recycle.

However, the use of PPA can probably be obviated entirely by the direct application of N_2O_5, provided the latter can be obtained at reasonable cost. This is now under study at Stanford Research International, Menlo Park, California (ref. 39).

7. Concurrently with the above program on the preparation of N_2O_5 and with the assumption that an economical procedure can be developed, it is proposed that an in-house study be initiated on its use in the third step. Preliminary work has already shown the feasibility of this concept, but a concerted R&D process study is needed to firmly establish reaction conditions and equipment requirements. The study would include determination of reaction rates, yields of HMX as a function of N_2O_5 concentration, and use of appropriate solvents. This program should require approximately ½ man-year.

8. At present, the only practical nitrolysis system for the third step is PPA-nitric acid. This system has seldom been used in the past, and has not been studied. It is important to determine the nature of the nitrolysis species present and the route by which it is formed. Such information could lead to substantial practical improvement in the nitrolysis step, and also possibly in the PPA recovery step. It is proposed to determine the nitrolysis species via N^{15} magnetic resonance spectroscopy. This study would require one man-year.

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APPENDIX A

MANUFACTURING TECHNOLOGY (MANTECH) PROGRAM

PROGRAM PROJECT STATUS REPORT (RCS DRCMT-301)

USA ARMAMENT RESEARCH AND DEVELOPMENT COMMAND,
DOVER, N.J. 07801

Report Date: 23 Jun 77

FINAL REPORT

1. Project No.: 5754277 (4932)

2. Project Title: New DADN Processes for HMX Manufacture

3. Period Covered: 16 Jan 75 - 31 May 77

4. Location of Work: ARRADCOM, Dover, NJ
Ofc of Proj Mgr for Prod Base Mod & Exp, Dover, NJ
United Technologies, Sunnyvale, CA
Los Alamos Scientific Laboratory, Los Alamos, NM

5. Project Officer: R. Motto, DRDAR-LCM-E, AV 880-3717

6. Funding Status:

See Inclosure 1

7. Milestone Chart:

See Inclosure 2

8. Item(s) Supported:

a. Major End Items: Items containing HMX such as the following:

Warhead, DRAGON, HE, M225 (Guided Missile)
Warhead, TOW, HE, M207 (Guided Missile)
Warhead, REDEYE, HE, M222 (Guided Missile)

b. Components Supported: N/A

c. Facilities Supported: None

d. Technical Area(s) Supported: Manufacture of HMX.

e. Requirements Supported: N/A

9. Task:

Develop a new process for the manufacture of HMX.

10. Project Objectives:

To completely demonstrate, characterize and optimize the DADN-HMX process and to gather sufficient engineering data and experience to support the design of a full scale prototype production facility.

11. Work Accomplished:

Under this program, work was accomplished at three sites, each investigating different phases of the DADN-HMX Process.

At ARRADCOM, the laboratory scale nitrolysis of hexamine to HMX via DAPT and DADN was investigated. This program climaxed with the preparation of 30 gm batches of HMX from DADN with separation and recycle of the nitrolysis media (polyphosphoric acid (PPA), nitric acid, and acetic acid formed during nitrolysis). Based upon information gathered at this site as well as that from the LASL reports on the same process, an economic evaluation of the process was prepared. The two major obstacles preventing the implementation of this process are the need of a radically new facility to produce HMX in lieu of the present Bachmann Process which produces either RDX or HMX, and the recycle of four separate acids; namely, nitric, acetic, sulfuric and polyphosphoric acids. The recycle and reconcentration of PPA to 83% P_2O_5 has not been accomplished commercially and based on data gathered from experts in the field, it may not be economically feasible. However, based upon laboratory results, vacuum concentration appears to be possible.

LASL investigated on a pilot scale (13.6 lb/hr) the continuous preparation of DADN via DAPT from hexamine. This task was successfully completed and an overall conversion rate of 95% was demonstrated for the nitrolysis of hexamine to DADN. Based upon the economic evaluation performed locally, LASL was asked to investigate the use of 93% H_2SO_4 in lieu of 98% acid. It was also confirmed by LASL that 93% sulfuric acid could be utilized in the nitrolysis of DAPT to DADN with no loss in yield. In an attempt to completely eliminate the use of sulfuric acid, the preparation of a different intermediate compound, namely, DANNO was investigated. Based upon the data generated, it was determined that the DANNO process offers no advantages over the DADN process. On the contrary, the DANNO approach entails increased nitrolysis times, excessive quenching, and generally lower yields, all of which negate the advantages gained from elimination of the sulfuric acid required in the DADN process. Therefore, this investigation was terminated. A final report compiling all the work accomplished at LASL has been published.

A twofold program was conducted by UT. The first phase consisted in the investigation of an inert carrier for the HMX via DADN process. Thirty-five pounds of DADN were produced in the pilot plant. The final run was for two hours and 40 minutes at a rate of 8.5 pounds per hour with an 86.5% yield

based on hexamine. Ten pounds of HMX were prepared with the final run for two hours at a rate of 3.5 pounds per hour and a yield of 67.5% based on DADN. An economic evaluation was prepared for the DADN-HMX system by UT. Based on UT data, the process appears to be competitive with the Bachmann Process; however, the same aforementioned obstacles exist to the implementation of this process.

The second phase of the UT program was to investigate the use of solvent-non-solvent recrystallization to produce coarse HMX. This phase, as designed, was not successful. However, an alternate method to produce fine particle (5μ) HMX was established. This process, in principle, is similar to the rapid quenching or aspirator methods utilized to shock HMX or RDX from solution. A final report on the work accomplished by UT has also been published.

12. Benefits:

a. Contractor technical reports documenting DADN-HMX manufacturing efforts via conventional and inert carrier processing techniques.

b. No patent rights are involved.

13. Implementation Procedures:

There are no plans to pursue this process further since it offers no advantages over the current improved Bachmann process.

14. Remarks:

None

6. Funding Status:

a. Project No.	5754277	5754277	5754277	5754277
Amount Authorized	$370.0	$25.0	$9.0	$12.7
Date Received	16 Jan 75	23 Jun 75	3 Feb 76	13 Apr 76
Date of Final Report	23 Jun 77			

b. Distribution of Funds:

(1) In-House Effort	Obligation FY75	Expenditure FY75
Labor	$63.3	$59.0
Material	0.0	0.0

(2) Contractor	Contr. No.	Date of Award	Contract Value FY75	Expenditure FY75
AEC LASL	AEC (W-7405-TNG-36)	18 Mar 75	$93.0	$93.0
UT	DAAA21-75-C 0251	9 Apr 76	257.7	250.0
GOCO				
Holston AAP	DAAA09-73-C	23 Jul 75	2.7	2.7
TOTAL			$416.7	$404.7

7. Milestone Chart:

Original FY	Phase	Initiated Sched/Act	Completed Sched/Act
75	Scope of Work	Nov 74/Nov 74	Feb 75/Feb 75
75	Award Contract	Feb 75/Feb 75	Apr 75/Apr 75
75	Concept Study (UT)	Apr 75/Apr 75	Feb 76/Feb 76
75	Feasibility Study (LASL)	Apr 75/Apr 75	Apr 76/Mar 76
75	Approval of Process for Piloting*	Mar 76/	May 76/
75	Final Report	Jan 77/May 77	Jan 77/Jun 77

*Milestone Deleted

Inclosure 2

APPENDIX B

COST ESTIMATE OF DADN-HMX PROCESS
3 January 1975
R. W. Hutchinson and R. Motto

Based on a February 73 preliminary cost estimate, the new DADN-HMX process appeared economically superior to the Bachmann HMX process utilized at Holston AAP. Since that time laboratory work has both improved parts of the process and invalidated some of the assumptions made in the preliminary estimate. In addition, significant improvements in the Bachmann HMX process were recently developed at Holston AAP. The following cost comparison between the DADN and Bachmann HMX processes reflects these changes and updates the earlier estimate.

Efforts have been made to compare the two processes on the same basis. For both processes, capital costs are based on an entirely new facility, and all costs are for crude HMX. With the emphasis on comparison, these estimates do not attempt to predict the present or future absolute cost of HMX.

The previous estimate, because of the low residence time expected for the DADN process, was based on HMX lines producing 4.5 mil lb./month. Laboratory results indicated that the residence times are nearly equal for the two processes, and hence, the processes should be compared at the same capacity per line. This comparison is based on two 0.5 mil lb. HMX/month lines as suggested by Mr. T. Caggiano, PM-PBM-EE. At this low capacity only one DADN production plant would be required. Flow diagrams for the two processes are shown in Figures 1 and 2. The number of reactors, etc. for each facility are indicated in the boxes.

A cost estimate for the DADN-HMX process at its present state of development is shown in Table I. The nitrolysis of DAPT to DADN currently requires the use of 98% sulfuric acid. Since sulfuric acid can be directly concentrated to only 93%, the purchase or production of oleum is required to strengthen the 93% acid to 98%. Production and purchase of oleum would require about equal daily expenditures, but the high capital cost of an oleum plant causes the purchase option to be favored. In the present case the acetic acid recovered from the spent sulfuric acid is very dilute (15%), and the cost to recycle this acid is high.

The operating cost estimate for an improved DADN-HMX process, the expected process, is presented in Table II. Improvements over the present case are the use of 93% rather than 98% sulfuric in DADN production and the recovery of concentrated acetic acid by flashing after the DAPT reaction. The improvements appear to have a good chance of success. Additional improvements which could lower the cost to $.75/lb.HMX would involve process changes, such as the elimination of sulfuric acid and improved HMX nitrolysis rates.

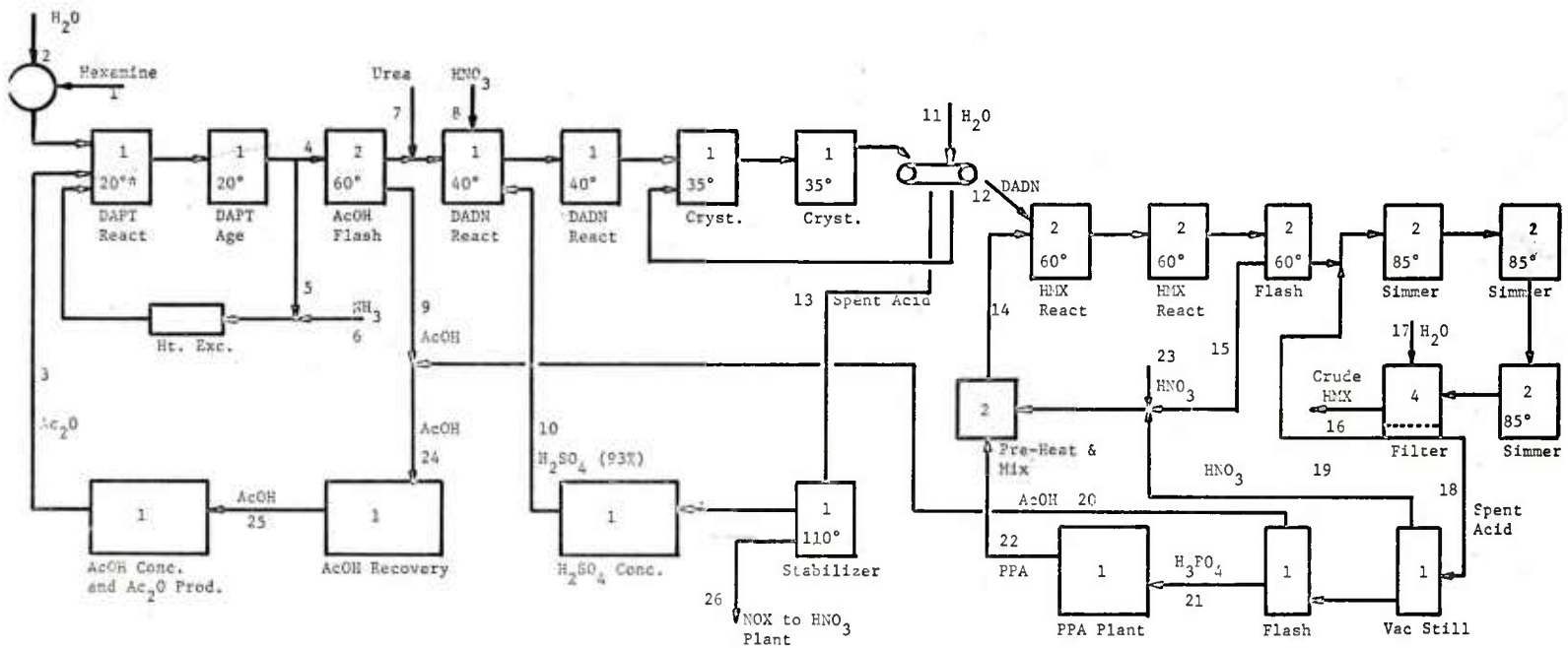
Cost estimates for the improved and standard Bachmann processes are shown in Tables III and IV, respectively. The expected DADN-HMX process offers a 19% cost savings over the improved Bachmann process. A 1973 cost estimate indicated that the DADN process might produce HMX for $.21/lb. as compared to $.63/lb. of HMX produced at Holston AAP by the standard Bachmann process. The DADN process offered a 66% cost savings over the Bachmann process.

The 1973 cost estimate is updated in Table V to indicate the factors most responsible for the cost increase of the expected DADN process. Material costs and acetic acid recycle costs increased uniformly for both the DADN and Bachmann processes. The cost for sulfuric acid recycle was not included in the previous estimate because of lack of data and presently adds 5¢/lb. HMX. The amount of PPA required to nitrate DADN to HMX is 7.4 times the value used in the preliminary estimate causing an 11¢/lb. HMX increase. The increased labor costs per manhour and the reduced scale of the lines result in the increased labor costs for making DADN and HMX.

Capital cost estimates for the expected DADN, improved Bachmann, and standard Bachmann processes in a 1 mil lb. HMX/month new facility are shown in Tables VI, VII, and VIII, respectively. The estimates for an independent plant would be for a totally self-sufficient facility; whereas, the integral HMX plants would be built in conjunction with a Bachmann RDX facility and would have common acetic acid and nitric acid areas. The latter case seems most likely for both DADN and Bachmann HMX facilities. Capital costs for the DADN and improved Bachmann plants appear to be the same.

Examples of cash flow tables for the DADN and Bachmann processes are presented in Tables IX and X, respectively. The cash flows include the cost of research and development, plant capital costs, and ten year production costs. The yearly discount rate is 10%. At these times when inflation equals interest, the undiscounted costs may be more valid than the discounted figures. Although the Bachmann plant could be built several years earlier than the DADN-HMX plant, in this comparison both plants are built and operated over the same periods so as not to unjustly penalize the Bachmann process in the discounted cash-flow analyses. It should be noted that capital costs tend to outweigh operating costs at the discounted values.

Table XI is a summary of operating costs, capital investment, and discounted cash flow totals for the DADN and Bachmann HMX processes. The costs are based on expected peacetime rates of 0.5 mm lb. HMX/month and mobilization rates of 1 mil lb. HMX/month as suggested by Mr. T. Caggiano, PM-PBM-EE. The DADN-HMX process does not appear to have a significant economic advantage over the improved Bachmann process at this time. Should the improved Bachmann process fail to be implemented in production, the DADN-HMX process would offer a discounted savings total of $20 mil at peacetime rates and $30 mil at mobilization rates.



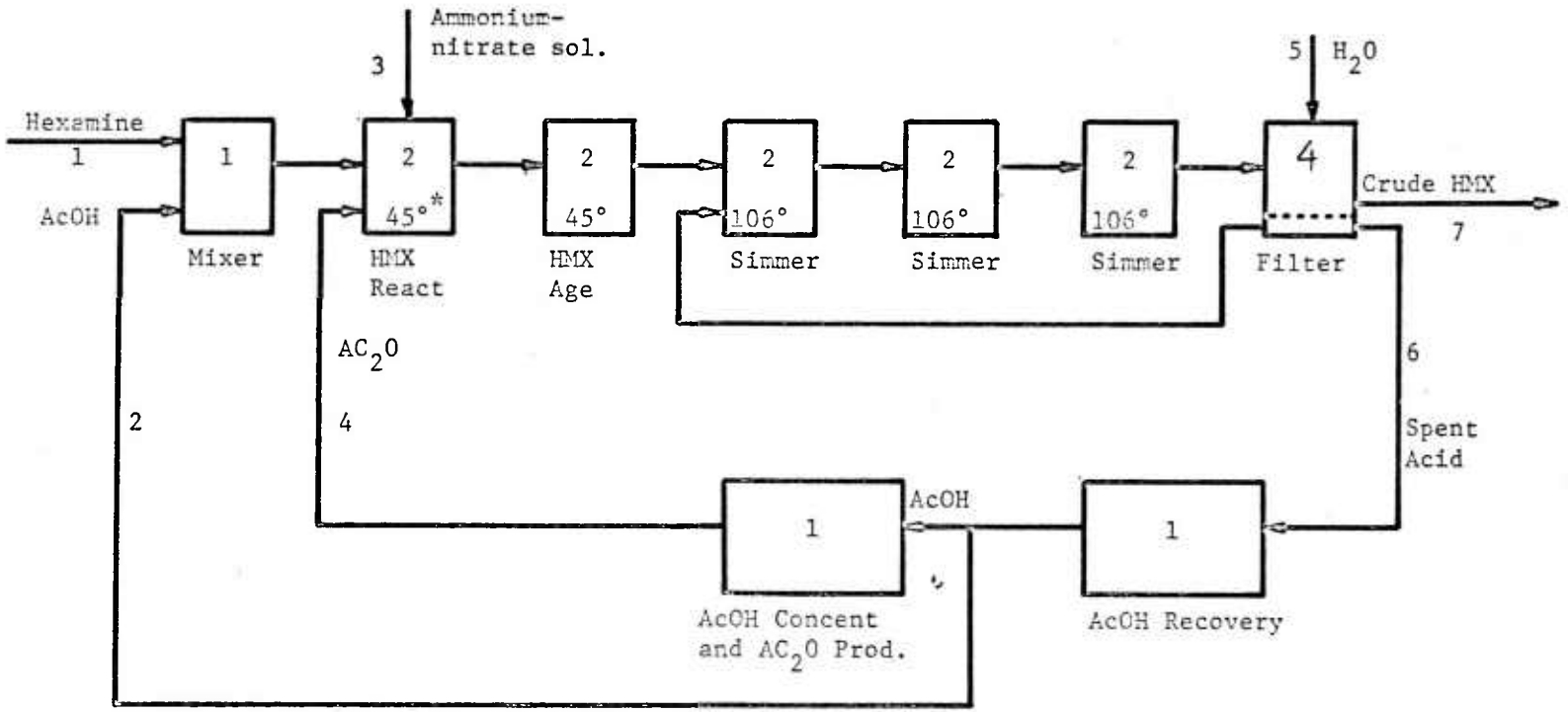
* Temperature in °C.

Figure 1. Flow diagram for expected DADN HMX process, 1 million pounds per month.

Stream #	1	2	3	4	5	6	7	8	9	10	11	12	13
Hexamine	15												
Urea							3						
DAPT				26	77								
DADN												29	
HMX													
HNO_3								21					
H_2SO_4										230			230
H_3PO_4													
AcOH			5	25	76				25.2				
AC_2O			27										
H_2O		7								17	213		230
NO_x													
NH_3						1.5							
PPA													

Stream #	14	15	16	17	18	19	20	21	22	23	24	25	26
Hexamine													
Urea													
DAPT													
DADN													
HMX			25										
HNO_3	108	44			38	38	.2			26			
H_2SO_4													
H_3PO_4					274			274					
AcOH					9.4		9.4				35	35	
AC_2O													
H_2O				34									
NO_x													4
NH_3													
PPA	240								240				

Figure 1. (Continued) Stream flow rates, pounds per hour.



* Temperature in °C.

Figure 2. Flow diagram for improved Bachmann HMX process, 1 million pounds per month.

Stream #	1	2	3	4	5	6	7
Hexamine	19						
AN Solution			70				
AcOH		61		27		125	
AC_2O				141			
HMX							25
H_2O					~80	83	

Figure 2. (Continued) Stream flow rates, pounds per hour.

TABLE I

PRODUCTION COST ESTIMATE FOR DADN-HMX PROCESS

Base-Case, Based on Present Laboratory Results

Material	¢/lb	lb/lb HMX	¢/lb HMX
Hexamine[1]	28.22	0.59	16.65
Acetic Acid Make-Up[1]	14.15	0.15	2.15
Sulfuric Acid Make-Up[2]	2.39	0.09	0.21
Urea[2]	8.00	0.12	0.96
Ammonia[1]	10.01	0.058	0.58
Nitric Acid[3]	4.39	2.02	8.89
Polyphosphoric Acid Make-Up[2]	9.08	0.29	2.63
40% Oleum (Net purchased)[4]	2.08	3.12	6.49
			38.56
Recycle			
Acetic Acid Recovery[5]	3.85	1.38	5.31
Acetic Acid Concentration[6]	4.43	1.54	6.82
Acetic Anhydride Production[6]	1.43	1.10	1.57
Nitric Acid[5]	0.29	3.28	0.95
Sulfuric Acid[7]	0.50	6.10	3.05
Polyphosphoric Acid[8]	1.18	9.61	11.34
			29.04
DADN Production (Labor,Maint.,Ovhd)[5]	10.9	1.15	12.54
HMX Production (Labor,Maint.,Ovhd)[5]			13.70
			$.93/lb HMX
Estimated Variation			+15%-5%

Source of Data:

1. HAAP letter dtd 2 Dec 74.
2. Chemical Marketing Reporter, Nov, 74.
3. Analogy to Hercules "Economic Evaluation of Candidate Processes for Manufacture of RDX", 1972.
4. RAAP Aug. 74 figure.
5. Engineering estimate by RWH, RM.
6. Tennessee Eastman Process described by SRI in "Eval. of Proc. for Cons. AcOH and Prod. Ac_2O", Cont. DAAA-21-72-6-0230 (Dec 72).
7. Information obtained from Mr. G. Colesian, Chemico Corp., 1 Penn Plaza, N.Y.C.
8. Data obtained from paper by W.C. Scott, G.G. Patterson, A.B. Phillips, Comm. Fertilizer & Plant Food Ind. (Aug 1966).

TABLE II

PRODUCTION COST ESTIMATE FOR DADN-HMX PROCESS

Expected Process with Acetic Acid Removal from DAPT Reactor and Use of 93% Sulfuric Acid in DADN Reaction.

Material	¢/lb	lb/lb HMX	¢/lb HMX
Hexamine[1,*]	28.22	0.59	16.65
Acetic Acid Make-Up[1]	14.15	0.15	2.15
Sulfuric Acid Make-up[2]	2.39	0.09	0.21
Urea[2]	8.00	0.12	0.96
Ammonia[1]	10.01	0.058	0.58
Nitric Acid[3]	4.39	2.02	8.89
Polyphosphoric Acid Make-Up[2]	9.08	0.29	2.63
			32.07
Recycle			
Acetic Acid Recovery[5]	1.85	1.38	2.55
Acetic Acid Concentration[6]	1.66	1.54	2.56
Acetic Anhydride Production[6]	1.41	1.10	1.55
Nitric Acid[5]	0.29	3.28	0.95
Sulfuric Acid[7]	0.50	9.20	4.60
Polyphosphoric Acid[8]	1.18	9.61	11.34
			23.55
DADN Production (Labor,Maint.,Ovhd)[5]	10.9	1.15	14.41
HMX Production (Labor,Maint.,Ovhd)[5]			13.20
			$.83/lb HMX
Estimated Variation			+15%, -5%

*Refer to Table I for footnotes.

TABLE III

PRODUCTION COST ESTIMATE FOR IMPROVED
BACHMANN PROCESS

Expected Process Based on HAAP Plant and Pilot-Plant Tests Using Reduced Amounts of Crude Acetic Anhydride (46% reduction) and Ammonium Nitrate (40% reduction).

Material	¢/lb	lb/lb HMX	¢/lb HMX
Hexamine[1,*]	28.22	0.71	20.04
Acetic Acid Make-Up[1]	14.15	0.34	4.81
Ammonium Nitrate Solution[1,3]	6.04	2.80	16.91
			41.76
Recycle			
Acetic Acid Recovery[5]	1.85	10.02	18.54
Acetic Acid Concentration[6]	1.66	10.78	17.89
Acetic Anhydride Production[6]	1.41	5.62	7.92
			44.35
HMX Production (Labor,Maint.,Ovhd)[5]			16.86
			$1.03/lb HMX
Estimated Variation			± 5%

*Refer to Table I for footnotes.

TABLE IV

PRODUCTION COST ESTIMATE FOR STANDARD BACHMANN PROCESS

HAAP Process Prior to FY75 Using Standard Amounts of Refined Acetic Anhydride and Ammonium Nitrate.

Material	¢/lb	lb/lb HMX	¢/lb HMX
Hexamine[1,*]	28.22	0.81	22.86
Acetic Acid Make-Up[1]	14.15	0.66	9.34
Ammonium Nitrate Solution[1,3]	6.04	3.40	20.54
			52.74
Recycle			
Acetic Acid Recovery[5]	1.68	16.03	26.93
Acetic Acid Concentration[6]	1.66	17.49	29.03
Acetic Anhydride Production[6]	1.41	10.82	15.26
Acetic Anhydride Purification[6]	0.66	10.82	7.14
			78.36
HMX Production (Labor,Maint.,Ovhd)[5]			16.86
			$1.48/lb HMX
Estimated Variation			± 5%

*Refer to Table I for footnotes.

TABLE V

UPDATE OF 1973 COST ESTIMATE FOR EXPECTED DADN HMX PROCESS

Material[1]	Mar 73 ¢/lb	Dec 74 ¢/lb	lb/lb HMX	Mar 73 ¢/lb HMX	Dec 74 ¢/lb HMX
Hexamine	9.50	28.22	0.60	5.70	16.93
AcOH	4.85	14.15	0.35	1.70	4.95
NH_3	1.78	10.01	0.06	0.11	0.60
HNO_3	1.05	4.39	1.19	1.25	5.22
				8.76	27.70
Recycle					
H_2SO_4 Consent.			?	-	4.60[2]
Acetic Anhydride	2.34	6.05[3]	1.31	3.07	7.92
Polyphosphoric Concent.					11.34[4]
Acid Separation				2.36	2.36
Labor,Ovhd,Maint				1.49	-[5]
				6.92	26.22
DADN (Labor,Maint.,Ovhd)				2.46¢	14.41[6]
HMX (Labor,Maint.,Ovhd)				2.78¢	13.20[7]
				$.21/lb HMX	$.82/lb HMX

Methods:

1. Material costs only are updated.
2. Use 93% H_2SO_4 in Dec 74 estimate.
3. Reflects increased utility and labor costs.
4. Reflects 7.4 fold increase in use of PPA over 72 value.
5. Labor, Ovhd, Maint. costs are included in each recycle cost for 74 estimate.
6. Reflects a decrease in line size to 1/4.5 that of 72 and increased labor rates.
7. Reflects a decrease in line size to 1/9 that of 72 and increased labor rates.

TABLE VI

CAPITAL COST ESTIMATE FOR DADN-HMX PROCESS

Two 0.5 mil lb HMX/Month Lines Designed for Expected DADN-HMX Process.

Area	Num. Units	Independent Plant, K$	Integral Plant, K$
Nitric Acid Production (Damag DSN)[1]	1	3,438	1,531
DADN Production[1,2]	1	6,174	6,174
DADN Dissolver[1]	2	1,902	1,902
HMX Production[1]	2	12,884	12,884
HMX Filter and Wash[1]	2	7,453	7,453
Acid Separation (Phosphoric, Sulfuric, Nitric)[2]	1	718	718
Phosphoric Acid Concentrator[3]	1	1,400	1,400
Sulfuric Acid Concentrator[4]	1	1,800	1,800
Acetic Acid Recovery[1]	1	1,238	440
Acetic Acid Concentration[5]	1	2,820	876
Acetic Anhydride Production[5]	1	2,518	549
Fertilizer Recovery[1]	1	1,260	738
Field Laboratory[1]	1	205	205
Tank Farms[1]		4,191	2,974
Sub total		48,001	39,644
Engineering, Support, Power and Utilities[1]		47,521	39,248
Total Facility Cost (1.99 x Sub Total[1])		96,000	79,000
Estimated Variation		± 20%	± 20%

Cost Method:

1. Analogy to DuPont "HMX/RDX Process Improvement Study", Contract No. DAAA09-68-C-0414, 1969.
2. Engineering estimate by R.W.H, R.M.
3. Data obtained from paper by W.C. Scott, G.G. Patterson, A.B. Phillips, Comm. Fertilizer & Plant Food Ind. (Aug 1966)
4. Information obtained from Mr. G. Colesian, Chemico Corp., 1 Penn Plaza, N.Y.C.
5. Tennessee Eastman Process described by SRI in "Eval. of Proc. for Comc. AcOH and AC_2O, Cont." DAAA-21-72-C-0230 (Dec 72).

TABLE VII

CAPITAL COST ESTIMATE FOR IMPROVED
BACHMANN HMX PROCESS

Two 0.5 mil lb HMX/Month Lines Designed for Reduced Usage of Crude Acetic Anhydride and Ammonium Nitrate.

Area	Num. Units	Independent Plant, K$	Integrated Plant, K$
Nitric Acid Production (Bamag DSN)[1]	1	4,034	1,999
Ammonium Nitrate Production[2]	1	500	250
Hexamine Dissolving[1]	1	1,900	1,900
HMX Production[1]	2	12,885	12,885
HMX Filter and Wash[1]	2	7,453	7,453
Acetic Acid Recovery[1]	1	4,059	3,189
Acetic Acid Concentration[3]	1	9,008	6,066
Acetic Anhydride Production[3]	1	6,653	2,773
Fertilizer Recovery[1]	1	1,586	1,084
Field Laboratory[1]	1	205	205
Tank Farm[1]		4,438	2,489
Sub Total		52,721	40,293
Engineering, Support, Power & Utilities[1]		52,194	39,890
Total Facility Cost (1.99 x Sub Total[1])		104,915	80,183
Estimated Variation		± 10%	± 10%

Cost Method:

1. Analogy to "DuPont HMX/RDX Process Improvement Study", Contract No. DAAA09-68-C-0414, 1969.
2. Estimate.
3. Analogy to SRI data presented in "Eval. of Proc. for Cons. of AcOH and Prod. of Ac_2O", Cont. DAAA-21-72-C-0230 (Dec 72).

TABLE VIII

CAPITAL COST ESTIMATE FOR STANDARD
BACHMANN HMX PROCESS

Two 0.5 mil lb HMX/Month Lines Designed for pre FY74 Usage of Refined Acetic Anhydride

Area	Num. Units	Independent Plant,K$	Integral Plant,K$
Nitric Acid Production (Bamag DSN)[1]	1	4,034	1,999
Ammonium Nitrate Production	1	500	250
Hexamine Dissolving[1]	1	1,900	1,900
HMX Production[1]	2	12,885	12,885
HMX Filter and Wash[1]	2	7,453	7,453
Acetic Acid Recovery[1]	1	5,375	5,091
Acetic Acid Concentration[3]	1	12,049	9,849
Acetic Anhydride Production[3]	1	9,872	5,355
Acetic Anhydride Purification[3]	1	3,989	2,164
Fertilizer Recovery[1]	1	1,586	1,084
Field Laboratory[1]	1	205	205
Tank Farm[1]		4,438	2,489
Sub Total		64,286	50,724
Engineering, Support, Power & Utilities[1]		63,643	50,217
Total Facility Cost(1.99xSub total[1])		127,929	100,941
Estimated Variation		± 10%	± 10%

Cost Method:

1. Analogy to DuPont "HMX/RDX Process Improvement Study", Contract No. DAAA09-68-C-0414, 1969.
2. Estimate.
3. Analogy to SRI data presented in "Eval. of Proc. for Cons. of AcOH and Prod. of Ac_2O", Cont. DAAA-21-72-C-0230 (Dec 72).

TABLE IX

ECONOMIC ANALYSIS COST SUMMARY

1. Submitting DOD Component: Picatinny Arsenal, Dover, NJ

2. Submission Date: 24 December 1974

3. Project Title: DADN HMX Process

4. Project Objective(s): Develop improved processes to produce HMX
Peacetime Production rates, HMX $0.83/lb

5. Project Alternative: DADN-HMX Process

6. Economic Life: 30 yr

7. 8. PROGRAM/PROJECT COSTS*

Project Year (FY)	Non-Recurring Costs a. R&D	b. Investments	c. Recurring/ Operating Costs	d. Annual Cost (Sum a,b,c)	e. Discount Factor	f. Discounted Annual Cost (d times c)
76	200[1]			200	0.954	191
77	2,000[2]			2,000	0.867	1,734
78	2,000[2]			2,000	0.788	1,576
79	2,000[2]			2,000	0.717	1,434
80	1,000[3]			1,000	0.652	652
81		26,297[4]		26,297	0.592	15,568
82		26,297[4]		26,297	0.538	14,148
83		26,297[4]		26,297	0.489	12,859
84			4,980[5]	4,980	0.445	2,216
85			4,980[5]	4,980	0.405	2,017
86			4,980[5]	4,980	0.368	1,833
87			4,980[5]	4,980	0.334	1,663
88			4,980[5]	4,980	0.304	1,514
89			4,980[5]	4,980	0.276	1,374
90			4,980[5]	4,980	0.251	1,250
91			4,980[5]	4,980	0.228	1,135
92			4,980[5]	4,980	0.208	1,036
93			4,980[5]	4,980	0.189	941
Totals	7,200	78,891	49,800	135,891	8.605	63,141

TABLE IX, Continued

Uniform Annual Cost ($\Sigma f \div \Sigma e$) = 7,338

*All costs are in thousands of dollars.

1. Laboratory and bench scale development.
2. Pilot plant development.
3. Design criterion.
4. Plant costs for an integral HMX and Bachmann RDX facility.
5. Operating costs for 0.5 mil lb HMX/month at $0.83/lb.

TABLE X

ECONOMIC ANALYSIS COST SUMMARY

1. Submitting DOD Component: Picatinny Arsenal, Dover, NJ

2. Submission Date: 24 December 1974

3. Project Title: DADN-HMX Process

4. Project Objective(s): Develop improved processes to produce HMX.

5. Alternative: Improved Bachmann HMX Process, Peacetime production rates, HMX $1.03/lb

6. Economic Life: 30 yr

7. 8 PROGRAM/PROJECT COSTS*

Project Year (FY)	Non-Recurring Costs a. R&D	Non-Recurring Costs b. Investments	c. Recurring/ Operating Costs	d. Annual Cost (Sum a,b,c)	e. Discount Factor	f. Discounted Annual Cost (d times c)
76	100[1]			100	0.954	95
77				-	0.867	-
78				-	0.788	-
79				-	0.717	-
80	1,000[2]			1,000	0.652	652
81		26,728[3]		26,728	0.592	15,823
82		26,728[3]		26,728	0.538	14,380
83		26,728[3]		26,728	0.489	13,070
84			6,180[4]	6,180	0.445	2,750
85			6,180[4]	6,180	0.405	2,503
86			6,180[4]	6,180	0.368	2,274
87			6,180[4]	6,180	0.334	2,064
88			6,180[4]	6,180	0.304	1,879
89			6,180[4]	6,180	0.276	1,706
90			6,180[4]	6,180	0.251	1,551
91			6,180[4]	6,180	0.228	1,409
92			6,180[4]	6,180	0.208	1,285
93			6,180[4]	6,180	0.189	1,168
Totals	1,100	80,184	61,800	143,084		62,609

TABLE X, Continued

Uniform Annual Cost ($\Sigma f \div \Sigma e$) = 7,276

*All costs are in thousands of dollars.

1. Process development for use of crude acetic anhydride.
2. Design criterion.
3. Plant costs for an integral HMX and Bachmann RDX facility.
4. Operating costs for 0.5 mil lb HMX/month at $1.03/lb

TABLE XI

Discounted Cash Flow for Building a One-Million lb/mo DADN or Bachmann HMX Facility and Operating the Facility for Ten Years[1].

Process	$/lb HMX[2]	Plant Cost[3,4]	Discounted Cash Flow[5,6,7] Low	Expected	High	Total Cash Expected
Case 1, Peacetime production at 0.5mm #HMX/month						
DADN(Present)	0.93	79	55	65	76	142
DADN(Expected)	0.83	79	54	63	74	136
DADN(Lowest)	0.75	75	51	60	70	128
Improved Bachmann	1.03	80	57	63	68	143
Standard Bachmann	1.48	101	75	82	89	191
Case 2, Mobilization production at 1.0mm #HMX/month						
DADN(Present)	0.93	79	71	82	95	198
DADN(Expected)	0.83	79	68	78	91	186
DADN(Lowest)	0.75	75	64	73	86	173
Improved Bachmann	1.03	80	75	81	87	205
Standard Bachmann	1.48	101	100	109	117	280

1. Plant and cash flows are in millions of dollars.
2. $/lb HMX could vary by +15%, -5% for DADN process and by ±5% for Bachmann.
3. Plant costs could vary by ±20% for DADN and ±10% for Bachmann.
4. Plant costs are for an integral HMX and RDX facility.
5. Costs are discounted at 10% per year.
6. Range reflects variances in $/lb HMX and Plant costs.
7. Uniform Annual Cost = Discounted Cash Flow figures ÷ 8.605.

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