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NATIONAL DEFENSE RESEARCH COMMITTEE

of the

OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

Report on "Studies on the Preparation and Properties of RDX"
to
August 15, 1942
by
W. E. Bachmann

OSRD No. 820

Serial No. 328

Copy No. 40

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Section B-2

Studies on the Preparation and Properties of RDX (OD-12)

by W. E. Bachmann

OSRD No. 820

Serial No. 328

August 24, 1942

Endorsement (1) from Dr. Ralph Connor, Technical Aide, Section B-2 to Dr. Roger Adams, Chairman, Division B.

> "This report describes the continuation of the work previously reported by Dr. Bachmann (Serial No. 88, OSRD No. 150). Important contributions have been made to (1) the knowledge of the proper conditions for controlling the yield and quality of RDX, (2) the recovery of the reagents, (3) the identity and characteristics of the by-products, (4) the purification of RDX. The results described here were the basis for many of the details of the pilot plant operations. The description of the pilot plant of the Western Cartridge Co. (Serial No. B-257, OSRD No. 612) has already been reported and the reports from the du Pont Company and the Tennessee Eastman Corporation will be issued shortly.

Serial No. 328

DIVISION B

NATIONAL DEFENSE RESEARCH COMMITTEE

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Section B-2

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Report on "Studies on the Preparation and Properties of RDX"
(OD-12)

Endorsement (1) from Dr. Ralph Connor, Technical Aide, Section B-2, to Dr. Roger Adams, Chairman, Division B. Forwarding report and noting:

> "This report describes the continuation of the work previously reported by Dr. Bachmann (Serial No. 88, OSRD No. 150). Important contributions have been made to (1) the knowledge of the proper conditions for controlling the yield and quality of RDX, (2) the recovery of the reagents, (3) the identity and characteristics of the by-products, (4) the purification of RDX. The results described here were the basis for many of the details of the pilot plant operations. The description of the pilot plant of the Western Cartridge Co. (Serial No. 3-257, OSRD No. 312) has already been reported and the reports from the Du Pont Company and the Tennessee Eastman Corporation will be issued shortly.

(2) Twenty-five copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee, as Progress Report under Contract (B-120, NDCrc 87) with the University of Michigan.

Roger Adams, Chairman
by Harris L. Chadwell
Technical Aide

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B. STUDIES ON THE PREPARATION AND PROPERTIES OF RDX

by

W. E. Bachmann
Official Investigator
National Defense Research Committee

Formal report on the work done
during the period
September 15, 1941--August 15, 1942
at the
University of Michigan

Copies to:

Dr. Ralph Connor..... 40 + stencils
File..... 2

Collaborators:

W. J. Horton
E. L. Jenner
N. W. MacNaughton

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ABSTRACT

The principles and conditions were determined for obtaining RDX (or RDX-HMX) in high quality and in excellent yield The RDX was prepared by the action of nitric acid, acetic anhydride, and ammonium nitrate on hexamine which was added in the solid form, in the form of the dinitrate, and also in acetic acid.

The processing of the product is described. Nearly pure RDX can be filtered directly from the reaction mixture or a mixture of RDX-HMX can be obtained by diluting the reaction mixture with water. In order to obtain a good product by the latter procedure and also to get the dilute acetic acid mother liquor in a better condition for recovery, it is recommended that the diluted reaction mixture be heated at 90-95° for a few hours.

An acetone and a nitromethane purification of the product were worked out which gave a product with an acidity, vacuum stability and ballistic power within the specifications.

The effect of various factors on the sensitivity of RDX-HMX mixtures is discussed.

A structure is proposed for the high-melting impurity, HMX, which accompanies the RDX.

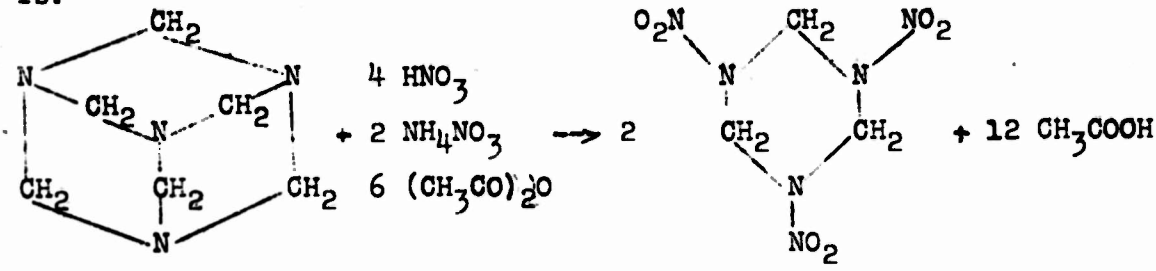
Some work is reported on the study of BSX, a substance which can be obtained from the same reagents used to prepare RDX.

THE PREPARATION AND PROCESSING OF RDX

Methods of Preparation

RDX from Hexamine Dinitrate

As described in our formal report of last year[1], conditions had been discovered whereby it was possible to obtain granular RDX of high quality and in good yield directly in the reaction mixture by the so-called combination process. In this new process, hexamine (solid or in acetic acid solution or as hexamine dinitrate) is treated with 98% nitric acid, ammonium nitrate and acetic anhydride between 50 and 80° to yield <u>two</u> moles of RDX per mole of hexamine. The overall equation is:



All of the factors had not been worked out, however, for occasionally a gelatinous mass would be obtained in the reaction flask which was difficult to stir and to filter. In the V-series of experiments, of which representative experiments are described below, a systematic study was undertaken to determine the conditions necessary for obtaining granular crystals of RDX. This study was successful.

In V-61, the experimental details of one of the successful procedures for preparing RDX from hexamine dinitrate are presented. The yield of RDX (m. p. 201-203° with previous softening), in the first crop (this term will be explained later) was 77% (based on two moles of RDX per mole of hexamine). The preparation of hexamine dinitrate from solid hexamine and from commercial hexamine solution is described first.

Hexamethylenetetramine Dinitrate.- A solution of 120 g. of hexamethylenetetramine in 210 cc. of water was prepared in a one-liter, wide-mouthed Erlenmeyer flask. The flask was placed in an ice-salt bath and the solution stirred mechanically while 130.5 cc. of 70% nitric acid was added at such a rate that the temperature did not rise above 15°. The solution was cooled to 5° and filtered (we centrifuged our product but suction may also be used). The solid adhering to the flask was washed into the filter with a small portion (20 to 40 cc.) of ice-cold 20% nitric acid. The product may be washed with acetone to facilitate drying but this is not necessary. The hexamethylenetetramine dinitrate is air dried at room temperature; yield, 217 g. (95%).

It was of interest to determine if the commercial hexamine solution could be used directly in the preparation of hexamine dinitrate without the previous isolation of the hexamine. We obtained from du Pont (R.&H.) a carboy of hexamine solution which we found to be 25.5% hexamine by weight.

A.- A 447 cc. sample of this solution was concentrated under reduced pressure to a volume of approximately 270 cc. To this was added (temperature kept under 15°), dropwise, 156 cc. of a 60% solution of nitric acid (a 19% excess). After cooling to 5°, the product was centrifuged and air dried. Yield, 214 g. (93%).

B.- In some experiments the 25.5% solution was used without concentration. For example: 300 cc. of the solution was treated in the cold with 95 cc. of 70% nitric acid (a 45% excess). The mixture was cooled to 5°, centrifuged, and the product air dried. Yield, 144 g. (94%).

These experiments indicate that it is feasible to obtain hexamine dinitrate directly from hexamine solutions.

V-61:- A five-necked, one-liter flask was used, (one neck for an efficient mechanical stirrer, one for the thermometer, two for burettes, and a large flanged one for the addition of solid). The flask was placed in a water bath not much larger in diameter than itself. This bath was equipped with a thermometer and could be heated by steam and cooled by running water.

Three men were required to regulate the addition and control the temperature for the reaction. Sixty-five grams of hexamine dinitrate was divided into 26 portions, (each portion was weighed into a dry test tube for convenience in handling; 160 cc. of acetic anhydride was placed in a burette calibrated in 27 portions; and 26 cc. of 98% nitric acid was placed in another burette calibrated in 27 portions.

At the beginning of the run, 20 g. of powdered ammonium nitrate and 15 cc. of glacial acetic acid were placed in the flask. The temperature was raised to 75° and two portions of acetic anhydride were

added. Vigorous stirring was started. After the addition of one-quarter portion of the dinitrate, (to act as an inhibitor), one portion of nitric acid was slowly added. The second portion of nitric acid was added simultaneously with the addition of the remainder of the first portion of dinitrate. The remaining twenty-five portions of the three reactants were then added equivalently and simultaneously over a period of about fifteen minutes. Five portions, (five grams each), of powdered ammonium nitrate were added at convenient intervals during the additions of the first ten portions. The temperature was maintained at 72-78° for the entire reaction.

The first man added the nitric acid and watched carefully the inside and outside temperatures, regulating the steam and cooling water. The second man added the acetic anhydride to correspond to the addition of the nitric acid and, watching the nitric acid burette, called off the addition in quarter-portions. The third man added the solid, hexamine dinitrate, to correspond to the additions of nitric acid; he added a quarter of the contents of the test tube at a time. The addition of the liquids was continuous and that of the solid effectively so, (i.e. in 100 quarter portions).

After the addition was complete, the mixture was stirred for fifteen minutes at the same temperature. The water bath was then removed and the mixture was allowed to cool to 60°, (about ten minutes were required). It was filtered through a warm coarse Jena funnel. The product was washed with 30 cc. of cold glacial acetic acid, and then with two 50 cc. portions of hot water. The air dried product was granular and of good appearance; yield 83.3 g. (77%); m. p. 201-203° corr., with previous softening.

The following table gives data on runs similar to V-61. It shows the effect of reagents and manner of addition on yield and quality.

Table I

Experiments Similar to V-61

In these experiments 65 g. of hexamine dinitrate, (DN), was used. In runs V-12 to V-33, the anhydride and nitric acid were previously mixed, (in the cold); in runs V-40 to V-60 they were added separately without mixing.

Abbreviations: AcOH= acetic acid; AN = ammonium nitrate; AcAn = acetic anhydride; DN = hexamine dinitrate; ML = mother liquor (not diluted with water) from a previous batch.

Theoretical Yield = 108.8 g.

Run No.	Yield first crop g.	M.P. °C corr.[a]	Nitric Acid, cc.[b]	AcAn cc.	AN added during reaction[c]	Material in flask at start
V-12	51.2	204-205°	26	160	39 g. mixed with DN	14 cc. mix.[d]
V-13	67.6	203-204°	26	160	" "	7 cc. mix.
V-14	77.0	196-199°	22	160	" "	" "
V-15	71.3	201-204°	26	160	" "	" "
V-21	67.1	203-204°	27	162	" "	14 cc. mix. 13 cc. AcAn
V-27	80.7	202-203°	23	166	45 g. mixed with DN	14 cc. mix. 13 cc. AcAn 5 g. AN
V-28	82.1	200-204°	24	160	15 g. after portion #8; 15 g. after #14	15 cc. AcOH 14 cc. mix. 20 g. AN
V-29	73.5	199-201°	22	160	~~39~~ g. mixed with DN	10 cc. AcOH 14 cc. mix. 11 g. AN
V-30	82.6	198-201°	24	160	" "	as in V-28
V-31	84.2	199-201°	25	160	as in V-28	as in V-28
V-32	82.9	200-202°	24	160	as in V-28	15 cc. ML[e] 14 cc. mix. 20 g. AN
V-33	79.6	198-200°	24	160	10 g. after portion #8; 9 g. after #14	as in V-28
V-34	81.0	201-203°	26	160	20 g. after portion #5	15 cc. ML 14 cc. mix. 25 g. AN
V-35	81.6	200-202°	26	160	none	15 cc. ML 14 cc. mix. 45 g. AN
V-36	85.7	198-200°	25	160	none	30 cc. ML 50 g. AN (or m.
V-40	80.9[i]	198-20[illegible]	27			

Table I (cont.)

V-41	81.8	198-200°	27	160	none	as in V-39
V-48[f]	85.8	198-203°	26	160	none	30 cc. ML 45 g. AN (gran.)
V-49[g]	81.4	199-203°	26	160	none	30 cc. ML 45 g. AN
V-50[h]	81.4	199-203°	26	160	none	as in V-48
V-60	84.6	201-203°	26	160	6 x 5-g. portions.	7 cc. AcOH 14 cc. AcAn 0.75 cc. HNO_3 15 g. AN

Notes: (a) With previous softening. (b) Volume of 98% nitric acid at 10°. (c) Powdered ammonium nitrate. (d) Solution of nitric acid in acetic anhydride. (e) Clear mother liquor from previous run. (f) Addition required 11 minutes; product was granular. (h) Addition required 18 mimutes; product was granular. (i) By accident solid was added one portion ahead of liquids.

Comments on Table I:- Experiments V-12, V-13 and V-15 show the results of being different amounts ahead on the addition of the liquid mixture, all three experiments used the same amount of nitric acid. V-14 used less total nitric acid, the result: lower quality, higher yield. V-27 and V-28 show that using more than the theoretical amount of ammonium nitrate results in an increased yield of good quality. A comparison of V-29 with V-30 shows that with 50 g. of ammonium nitrate, 24 cc. of nitric acid produced a higher yield than did 22 cc. A comparison of V-28 with V-30 shows that the quality is distinctly better when the ammonium nitrate is added in the early part of the reaction. The high yield (80%) and the low quality of V-40 show the drastic effect of adding the solid (hexamine dinitrate)

before the addition of the corresponding amount of the liquid reagents. An examination of V-48, V-49 and V-50 leads one to conclude that (a) if a run with coarse ammonium nitrate is carried out slowly (V-50) the results are the same as using fine ammonium nitrate and operating more rapidly (V-49); however (b) if the run with the coarse ammonium nitrate is at the same rate as that with the fine, the yield is higher but the product is inferior (V-48).

The V-61 technique is quite satisfactory from the standpoint of yield and quality. However, because of the small volume in the flask at the beginning of the reaction, control is difficult, a difficulty that might become more marked on a larger scale. For this reason we conducted a series of experiments with the object of maintaining the yield and quality but using a larger charge in the flask at the beginning of the reaction. V-86 is the result of this work. The initial charge has been doubled and the yield and quality are still good.

V-86:- The general technique is the same as that described for V-61. The hexamine dinitrate used, (65 g.) was divided into 26 portions. One hundred and forty-five cc. of acetic anhydride was placed in a burette calibrated in 26 portions, and 26 cc. of 98% nitric acid was placed in another burette calibrated in 28 portions.

At the beginning of the run, 50 g. of dry ammonium nitrate (60-120 mesh) and 30 cc. of glacial acetic acid were placed in the flask. The temperature was raised to 75° and 30 cc. of acetic anhydride was added, (this was 30 cc. in addition to the 145 cc. in the burette). The resulting mixture was fluid and quite easily stirred. After the addition of one-quarter portion of the dinitrate (to act as inhibitor), two portions of nitric acid were slowly added. The third portion of nitric acid was then added simultaneously with the remainder of the first portion of dinitrate and the first portion of acetic anhydride.

The remaining 25 portions of the three reagents were then added equivalently and simultaneously over a period of about twelve minutes. The temperature within the flask was maintained at 74-76° throughout the addition.

After the addition was complete, the mixture was stirred for fifteen minutes at the same temperature, and then allowed to cool to 60° and filtered and washed. Yield, 81.8 g.; m. p. 201-203° (corr.).

Table II gives data on runs similar to V-86.

Table II

Experiments Similar to V-86

All of these runs required approximately fifteen minutes for the addition of the reactants. The temperature throughout was maintained at 74-76°. In all of the experiments except V-87 and V-88 there was 50 g. of powdered ammonium nitrate in the flask at the beginning. All experiments employed 65 g. of hexamine dinitrate divided into 26 portions. The runs were started with 30 cc. of acetic acid and 30 cc. of acetic anhydride in the flask. The quantity of anhydride listed in the table does not include the 30 cc. in the flask at the start.

Theoretical Yield, 106.8 g.

Run No.	Yield first crop g.	M. p. °C. (corr.)[a]	AcAn cc.	Total cc. of nitric acid	Cc. of nitric acid in flask at start
V-70	72.0	203-205 (198)	145	26 C[b]	3
V-71	76.4	202-204 (195)	145	27 C	2
V-72	78.5	202-204 (195)	145	26 C	2
V-73	82.0	202-203 (195)	145	26 R	1.5
V-76	84.0	199-203 (190)	130	26 R	2
V-77	81.5	199-203 (190)	130	26 R	3
V-78	76.6	201-204 (195)	130	27 R	3
V-83	80.5	199-203 (193)	145	26 R	2[c]
V-84	76.7	202-204 (197)	145	26 C	2
V-86	84.1	201-203 (196)	145	26 R	2
V-87	80.7	202-203 (196)	145	26 R	2[d]
V-88	83.0	201-204 (196)	130	26 R	2[e]

(a) Softening points are given in parentheses.

(b) The letter "C" indicates that the volume was measured at 10°; "R" indicates that the volume was measured at 25°.

(c) At the beginning of the reaction, the 2 cc. of nitric acid were added to the acetic acid before the 30 cc. of acetic anhydride were added.

(d) A total of 45 g. of ammonium nitrate was used; 25 g. was in at the start and 20 g. additional was added over the addition of the first eight portions.

(e) Ammonium nitrate added as in note (d). All of the acetic anhydride was added before the addition of portion #20.

Comments on Table II:- Experiments V-70, V-71 and V-72 show how the quality depends directly, and the yield inversely upon the quantity of nitric acid. A comparison of V-76 and V-86 shows how the quantity of acetic anhydride may have the same effects upon yield and quality. Runs V-87 and V-88 indicate that less than 50 g. of ammonium nitrate may be sufficient. Run V-88 indicates that it may be of value to add the acetic anhydride during the earlier part of the reaction (cf. V-76).

During the summer months we kept the nitric acid in a cold place to prevent its decomposition. When this nitric acid was used the volume was measured at 10°. Since V-73 the majority of our experiments were performed with nitric acid at room temperature. These volumes were measured at about 25°. We have found the results to differ appreciably depending on the temperature of the nitric acid when it was measured out. In Table II we have specified whether the acid used was cold or at room temperature.

During the previous year RDX had been prepared not only from hexamine dinitrate but also from solid hexamine and from hexamine in acetic acid solution* (presumably as the hexamine diacetate). The procedures with solid hexamine corresponded to those in which the dinitrate was employed. With hexamine dissolved in acetic acid, the preparation was carried out by adding gradually the two solutions, (1) hexamine in acetic acid and (2) nitric acid, to ammonium nitrate and acetic anhydride (62% yield)** The conditions which were worked out for the preparation of high quality RDX from hexamine dinitrate were found to be applicable now to the preparation of RDX from hexamine or from a solution of hexamine in acetic acid.

From Solid Hexamine:- In V-46 are given the details of a preparation of RDX using solid hexamine. For the liquid in the flask a certain amount of mother liquor (not diluted with water) was used which had been obtained in a previous run by filtering the solid RDX from the cooled reaction mixture. Mother liquor was employed in order to eliminate the use of fresh acetic acid and thus eliminate a certain amount of the recovery of this reagent. The procedure also represented a preliminary step toward a continuous method of operation. Mother liquor was used in all of the experiments listed in Table III except V-118 and V-119 in which a mixture of acetic acid and acetic anhydride was used in the pot.

V-46:- The procedure was the same as that employed in V-61 (page 3). The hexamine (33.6 g.) was divided into 26 portions. One

* Dr. G. F. Wright at the University of Toronto was the first to use a solution of hexamine in acetic acid.

** This procedure was inadvertently omitted from the formal report of last year.

hundred and thirty cc. of acetic anhydride was placed in a burette calibrated in 26 portions and 41 cc. of 98% nitric acid was placed in another burette calibrated in 26 portions.

At the beginning of the run 65 g. of ammonium nitrate and 30 cc. of mother liquor from a previous run were placed in the flask. The temperature was raised to 75° and 30 cc. of acetic anhydride, (this is 30 cc. in addition to the 130 cc. of acetic anhydride in the burette), is added. The addition of the two liquid and solid reagents is then started simultaneously. The reagents are added equivalently over a period of about fifteen minutes. The product is aged and cooled as before to 60°, filtered, washed and dried. Yield 75.4 g. (first crop); m.p. 200-203° (corr.).

Table III

Representative Experiments Using Solid Hexamine

All of these experiments used 33.6 g. of solid hexamine and 160 cc of acetic anhydride and were run by the procedure described in V-46. The addition of the reagents required approximately fifteen minutes. The temperature was maintained at 73-77° during the reaction. In all of the runs, except V-118 and V-121, 30 cc. of the cool, clear mother liquor from a previous run was placed in the flask with the ammonium nitrate before the other reagents were added. The addition of the liquid and of the solid reagents started at the same time except in runs V-53 and V-54 where the liquids had one portion added before the addition of solid commenced.

Theoretical Yield = 106.8 g.

Run NO.	Yield first crop g.	M.p. °C corr.	Nitric Acid cc.	Ammonium Nitrate g.
V-42	57.8	201-204°	47	50 g. in at start
V-43	64.8	201-203°	43	" "
V-47	78.2	197-202°	43	50 g. in at start 25 g. added after portion #5
V-53	69.6	199-202°	41[a]	65 g. in at start
V-54	66.9	202-205°	43[a]	as in V-47
V-118[b]	68.6	198-202°	42	as in V-53
V-121[c]	66.2	198-203°	43	" "

(a) One portion ahead on the addition of the liquids.

(b) Ran in 50 minutes; total of 175 cc. of acetic anhydride used. Pot contained 30 cc. of acetic anhydride along with the ammonium nitrate.

(c) Total of 175 cc. of acetic anhydride used. Pot contained 30 cc. of acetic anhydride along with the ammonium nitrate.

Comments on Table III: Higher yields were obtained when less nitric acid was used than would be calculated from the experiments on the dinitrate. A larger amount of ammonium nitrate appears to be desirable than is used with hexamine dinitrate. A comparison of V-47 and V-54 shows the tremendous difference caused by being one portion ahead on the liquids, acetic anhydride and nitric acid, relative to the addition of the hexamine. More efficient cooling is needed with hexamine than with hexamine dinitrate.

Hexamine in Acetic Acid.- The following variations of the procedure were employed (arrows signify "added to").

Procedure	Solutions in burettes		Material in reaction flask
A	1) Hexamine in AcOH 2) 98% Nitric acid	⟶ ⟶	Suspension of ammonium nitrate in acetic anhydride
B	1) Hexamine in AcOH 2) 98% Nitric acid 3) Acetic anhydride	⟶ ⟶ ⟶	Suspension of ammonium nitrate in AcOH (small amount) and some acetic anhydride
C	1) Hexamine in AcOH 2) Ammonium nitrate in nitric acid 3) Acetic anhydride	⟶ ⟶ ⟶	Mother liquor or simulated mother liquor (AcOH and acetic anhydride)

Only a few runs (V-123 and V-128) were made employing procedure A (a procedure which Dr. J. R. Johnson has studied extensively). We obtained somewhat better results by procedure B and variations which represented a compromise between A and B. The results of representative experiments are given in Table IV. The experimental details of an experiment employing procedure B are given in V-129.

Example of Procedure B (V-129).- The operations were carried out in the manner described in V-61.

A solution was prepared containing 33.6 g. of hexamine dissolved in 55.0 g. of glacial acetic acid (actually ten times this amount was prepared). The burette was filled with about half again the amount required for one run. The burette was calibrated from near the top to deliver the 88.6 g. of solution in 25 equal portions. Thus it was not necessary to drain the last third of the somewhat viscous solution from the burette. A second burette was filled with 80 cc. of acetic anhydride and calibrated in 25 portions. The third burette was filled with 47 cc. of 98% nitric acid, 45 cc. divided into 25 equal portions and the other 2 cc. to be added at the beginning of the reaction.

At the beginning of the run, 65 g. of dry ammonium nitrate and 30 cc. of glacial acetic acid were placed in the flask. The temperature of the water bath was raised to 80° and 80 cc. of acetic anhydride was added. When the internal temperature had risen to 65°, 0.5 cc. of the hexamine solution was added and then 2 cc. of nitric acid. The twenty-five portions of the three reagents were then added simultaneously over a period of thirteen minutes, maintaining the temperature at 75-75°. The product was aged, cooled to 60°, filtered, washed and dried. Yield, 72 g. (68%); m. p. 199-203° (corr.).

The hot filtrate was diluted with 630 cc. of hot water and heated for three hours on a steam bath. The mixture was cooled to room temperature and filtered. Yield of second crop, 12.7 g.; m. p. 190-197° (corr.). Total yield 84.7 g. (80%).

Table IV

Experiments Using Hexamine Solution

(Procedures A and B)

Theoretical Yield, 106.8 g.

Run No.	Yield, total g.	Yield[a] crops g.	M. p., °C, (corr.)[b]	Nitric acid;[c] AcAn, cc.	Material in flask[d] at start of the reaction
V-120	81.2	1) 63.1 2) 18.1	199-203 191-197	43-0 130	60 cc. AcAn; 65 g. AN
V-123	76.0	1) 63.4 2) 12.6	198-202 190-194	43-0 None	160 cc. AcAn; 65 g. AN
V-124	81.1	1) 67.8 2) 13.3	198-202 189-195	43-0 60[e]	100 cc. AcAn; 65 g. AN
V-125	80.4	1) 68.7 2) 11.7	195-201 188-198	43-0 100[e]	30 cc. AcOH; 60 cc. AcAn; 65 g. AN
V-126	85.6	1) 71.1 2) 14.5	200-203 190-198	47-4 100[e]	100 cc. AcOH; 60 cc. AcAn; 75 g. AN
V-127	83.6	1) 72.9 2) 10.7	195-201 190-200	44-1 80	30 cc. AcOH; 80 cc. 80 cc. AcAn; 65 g. AN

Table IV (continued)

V-128	82.8	1) 68.6 2) 14.2	199-203 191-199	47-4 none	100 cc. AcOH; 160 cc. AcAn; 65 g. AN
V-129	84.7	1) 72.0 2) 12.7	199-203 190-197	47-2 80	30 cc. AcOH; 80 cc. AcAn; 65 g. AN
V-130	82.0	1) 70.0 2) 12.0	198-203 191-195	47-2[e] 80	as in V-129
V-131	82.8	1) see 2) 2) 82.8	 196-202	47-2 80	as in V-129
V-139	86.6	1) 71.7 2) 14.9	199-203 195-202	47-2 100	100 cc. AcOH; 60 cc. AcAn; 65 g. AN
V-140	86.4	1) 73.6 2) 12.8	200-204 194-201	47-2 110	30cc. AcOH; 60 cc. AcAn; 65 g. AN
V-142	86.0	1) 73.3 2) 12.7	200-203 190-197	47-2 110	as in V-140
V-143	83.4	1) 71.3 2) 12.1	201-204 194-200	50-3 110	as in V-140
V-146	88.4	1) 77.5 2) 10.9	199-202 -------	47-2 140	30 cc. AcOH; 30 cc. AcAn; 65 g. AN
V-147	88.0	1) 78.0 2) 10.0	199-202 193-204	47-2 140	30 cc. AcOH; 30 cc. AcAn; 50 g. AN
V-148	----	1) 69.4 2) ----	201-203 -------	50-3 140	as in V-147
V-149	88.0	1) see 2) 2) 88.0	------- 195-202	47-2 140	as in V-147
V-150	----	1) 74.1 2) ----	201-203 -------	47-2[f] 140	as in V-147
V-151	----	1) 78.5 2) ----	196-202 -------	47-2 140	as in V-147

All experiments are identical with V-129 except as noted.

Notes:- (a) Following "1" are the weight and m. p. of the first crop; "2" is the second crop. See description of V-129 regarding the first and second crop. (b) With previous softening. (c) The first number is the total cc. of nitric acid used; following the hyphen is the number of cc. added before the equivalent addition of the three reagents commences; the bottom number is the cc. of acetic anhydride added. (d) See Table I for the abbreviations used. (e) All acetic anhydride added during the first six minutes. (f) Addition required 25 minutes, reaction run at 65°

In procedure C the ammonium nitrate is added in the form of a solution in 98% nitric acid. As a result all of the reagents employed in the reaction are added in the form of liquids. After this procedure had been devised, we learned that Dr. G. F. Wright had used it earlier.

When ammonium nitrate is dissolved in yellowish 98% nitric acid, gassing occurs. This ceases after a short time and a nearly colorless solution results (with the proportions given in the experiment).

In previous experiments in which a small amount of 98% nitric acid was added to acetic anhydride in the reaction flask at the start of a run, it was observed that a rather violent reaction was likely to take place when the mixture was kept too long at 70-80° before the addition of the other reagents was started. A small amount of hexamine, free or in the forms of its dinitrate (or diacetate) was found to inhibit this[11h] desirable reaction. It was observed that a mixture of acetic anhydride and the solution of ammonium nitrate in nitric acid used in the experiments did not readily give rise to the violent reaction (at least it was greatly delayed) so that no hexamine needed to be added as an inhibitor.

The experimental details for the procedure C are given in V-167.

Example of Procedure C (V-167).- Fifty-five g. of ammonium nitrate was dissolved in 75 g. of 98% nitric acid and, after gassing had ceased, the solution was cooled to room temperature. The hexamine solution was prepared as in V-129; for the experiment 89.6 g. of the acetic acid solution containing 33.6 g. of hexamine was employed. The ammonium nitrate-nitric acid solution was placed in a burette calibrated in 25 equal portions plus one 6-cc. portion. The acetic anhydride (150 cc.) was placed in another burette calibrated in 25 portions.

At the start, 30 cc. of glacial acetic acid and 30 cc. of acetic anhydride were placed in the flask. After the temperature had been raised to 75°, 6 cc. of the ammonium nitrate-nitric acid solution was added from the burette. The three liquids in the burettes were then added portion for portion simultaneously over a period of thirteen minutes. The temperature was maintained at 73-75° and the mixture was stirred vigorously throughout the reaction. The mixture was stirred at that temperature for ten minutes, then allowed to cool to 60° and filtered. Yield 70.7 g. (first crop); m.p. 201-203° (corr.).

In another run the reaction mixture was diluted with 600 cc. of hot water and the well stirred reaction mixture was allowed to cool to 20° and filtered. Yield 84.1 g. m.p. 197-202° (corr.).

In still another run the reaction mixture without dilution with water was stirred as it cooled to 20°; the product filtered, and washed with hot water. Yield, 79.7 g.; m.p. 199-202°.

Procedures for preparing RDX using less ammonium nitrate.- If it is difficult to recover the excess ammonium nitrate used in the preparation of RDX it becomes of prime importance to reduce the excess ammonium nitrate used to a minimum. We have conducted a series of experiments using the ammonium nitrate dissolved in the nitric acid with the aim of cutting down the ammonium nitrate.

The following five experiments are cited as typical of the results obtained when less ammonium nitrate is employed.

Table V

Experiments Using Less Ammonium Nitrate

All of these experiments are by the same general procedure as described for V-167. The ammonium nitrate was dissolved in nitric acid. In all cases 33.6 g. of hexamine dissolved in 50 g. of acetic acid was employed. The RDX was isolated by filtering the undiluted mother liquor at 60°.

Run No.	First crop[a] g.	M.p. °C (corr.)	Reagents added		Material in flask at the start
V-152	74.2	201-203°	55 g. AN 72 g. nitric acid 165 cc AcAn	2[b]	5 cc. AcAn 25 cc. AcOH
V-153[c]	72.8	201-203°	50 g. AN 72 g. nitric acid 145 cc. AcAn	4	30 cc. AcAn 30 cc. AcOH 5 g. AN
V-160	71.5	200-203°	5 . AN 7 . nitric acid c . AcAn	6	30 cc. AcAn 30 cc. AcOH
V-161[c]	70.9	201-203°	5 . AN 75 g. nitric acid 140 cc. AcAn	6	30 cc. AcAn 30 cc. AcOH
V-163	77.5	199-20	50 g. AN 70 g. nitric acid 140 cc. AcAn	6	30 cc. AcAn 30 cc. AcOH

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Notes: (a) Approximately 10 g. should be added to these values to get the total or single crop yield. (b) This is the number of cc.'s of the ammonium nitrate-nitric acid solution added to the flask before the simultaneous addition of the three reagents commences. For the abbreviations used, see TableI. (c) The product from V-153 and V-161 filtered well. In the other runs there was a small amount of very fine material which caused the filtration to be slow.

These five experiments indicate that it may be possible to develope a satistfactory procedure for the preparation of RDX using well under 60 g. of ammonium nitrate.

Effect of Various Factors on Yield and Quality of RDX

Amounts and Concentration of Reagents.- It was found that in general the mixture should contain throughout the reaction;

1) Some excess of nitric acid
2) Some excess of acetic anhydride
3) Some excess of ammonium nitrate

These statements apply to the initial mixture in the pot at the start of the reaction as well as to the reaction mixture during the reaction. In order to obtain the proper conditions, some nitric acid and acetic anhydride and ammonium nitrate were generally added to acetic acid in the pot before the run was started. Usually the concentrations were these which prevail in the mother liquor at the end of the run. It is especially important that the nitric acid concentration be maintained.

If too little nitric acid is employed or if no nitric acid is present, a gelatinous product is formed which is difficult to stir and difficult to filter. A large excess of nitric acid results in exceptionally high quality RDX but in a lower yield, so there exists a more or less optimum concentration of this reagent.

It was our experience that it is best to avoid too great a concentration of acetic anhydride in the reaction mixture. For this reason we preferred, for example procedure B over A (page 12) in which the acetic anhydride is added gradually along with the other reagents to the reaction pot, rather than have it all in the pot at

the start of the reaction. Too much acetic anhydride seemed to result in a decreased yield. One reason for this may be the fact that ammonium nitrate is not very soluble in acetic anhydride.

If the amount of ammonium nitrate is too small, the yield of product drops. With a larger amount of ammonium nitrate a greater amount of nitric acid can be tolerated by the reaction mixture, which results in a high yield of good quality RDX.

Effect of Time and Temperature.- In all work previously reported, fifteen minutes was more or less the standard time of reaction for the amount of hexamine (33.6 g. or the equivalent amount of dinitrate) used in the runs. Anticipating difficulty in adding reagents in that time on a larger scale, we carried out a number of experiments in which the time of addition of reagents was greatly increased.

In general we found that satistfactory results can be obtained in slow runs provided a lower reaction temperature is used. The following table shows the results obtained.

Table VI

Theoretical Yield, 106.8 g.

Run No.		Yield first crop, g.	M.p.°C (corr.)	Time of Addition (minutes)	Temp. of Reaction	Nitric Acid cc.
V-36	(a)	78.6	202-204°	34	75°	26
V-94	(a)	78.9	200-203°	24	75°	26
V-98A	(a)	73.3	201-203°	54	75°	26
V-98B	(a)	65.7	202-204°	54	75°	26
V-99	(a)	74.8	202-204°	50	75°	25
V-100	(a)	79.0	202-204°	50	65°	25
V-101	(a)	74.5	202-204°	50	55°	25
V-102	(a)	76.4	-----	105	65°	25
V-86C	(a)	72.0	201-203°	120	65°	25

Table VI (cont.)

V-103	(a)	78.2	202.5-204.5°	60	67°	24
V-105	(a)	83.5	199-201°	13	65°	25
V-106	(a)	76.6	201-203°	50	65°	26
V-107	(a)	70.3	201.5-203.5°	100	75°	25
V-108	(b)	66.4	198-202°	60	65°	41
V-116	(a)	77.1	201-203°	25	70°	26
V-118	(b)	68.6	198-202°	50	65°	41
V-150	(c)	74.1	201-203°	25	65°	47
V-187	(d)	63.7°	193-195°	25	65°	41
V-188	(d)	59.7°	199-201°	6	75°	41

Notes.- (a) Hexamine dinitrate was the reagent used (procedure V-61). (b) Solid hexamine was used (procedure V-46). (c) Hexamine dissolved in acetic acid was used (procedure B). (d) The hexamine was dissolved in acetic acid and the ammonium nitrate was dissolved in 98% nitric acid. (e) Total crop.

Processing of RDX

Filtration of RDX from the Reaction Mixture.- In a great many experiments the reaction mixture, containing suspended RDX, was cooled to 60° and then filtered at this temperature. The product on the filter (so-called first crop) was usually in the form of glistening crystals and was high quality RDX, practically free from HMX. Its m.p. was usually above 200° and its sensitivity corresponded to that of RDX prepared by the direct nitration of hexamine.

From the filtrate a second crop of product was obtained usually by addition of water, followed by digestion at 95°. This material

contained appreciable amounts of HMX and unless submitted to a special treatment (to be described later) was abnormally sensitive in the impact test.

By employing the filtration at 60°, the yield of product formed in the reaction was determined (although only the first crop was weighed; the second crop usually amounted to about 10 g.) much more rapidly than the case when the entire product was obtained by dilution of the reaction mixture with water, simmering, cooling, etc. Moreover, by working up the filtrate separately from the solid phase, the technique was discovered for getting a second crop in an excellent crystalline form, and this technique was then employed when the entire reaction mixture was diluted.

Dilution and Digestion at 95°:- When the total product was to be isolated, the reaction mixture at 60-70° was diluted with water until the acetic acid concentration was reduced to 30-50%, the mixture was then heated on a steam bath (internal temperature 90-95°) for an hour or more, then the mixture was allowed to cool spontaneously with vigorous stirring. The resulting product filtered with ease.

It had been found that if the diluted mother liquor was not heated for some time, the product which was thrown out of solution by the water was in a poor condition for filtration. Moreover, when the filtrate was evaporated under reduced pressure, in order to recover the acetic acid, a water-insoluble oil appeared in the flask during the last stages of the distillation. This oil (which was decomposed by hot aqueous acid, giving off formaldehyde as one of the products) did not appear if the diluted mother liquor had been heated at 90-95° for at least one hour. Accordingly, the simmering technique was employed in the future.

Cooling with Stirring:- As will be discussed in the section

onsensitivity, a sensitive product results if a hot mixture of RDX and HMX in 30-50% acetic acid is allowed to cool spontaneously without stirring. If, however, the mixture is stirred vigorously during the cooling process, the product possesses normal sensitivity.

Purification of the Product

The product which was obtained by the operations described above was unsatisfactory from the standpoint of acidity and vacuum stability. A satisfactory product was obtained by dissolving the product in acetone or nitromethane and then passing steam into the solution until all of the organic solvent was removed.

Purification by an Acetone Treatment.- Fifty grams of crude RDX (acidity, 0.25%) was dissolved in 500 cc. of hot acetone, and steam was passed into the solution till all of the acetone had been removed. About 250 cc. of water was present at the end of this operation. The product was filtered from the cooled reaction mixture. Yield, 48.9 g.; acidity, 0.02%. The acetone in the distillate was fractionated and reused. As will be shown later, it is necessary to remove the acetone in a leisurely fashion (about three hours) with vigorous stirring during this operation and during the cooling process.

Purification by Means of Nitromethane.- Ten grams of crude material was dissolved in 40 cc. of hot nitromethane. It was heated with 5 cc. of water on the steam bath for three hours. Twenty-five cc. of warm water was added and the mixture distilled under a slight vacuum. Twenty-five cc. more of water was added and after cooling the mixture was filtered. Yield, almost quantitative. Acidity, 0.02%. The nitromethane is separated from the water in the distillate and reused.

An alternative method of purification is to suspend the crude material in a Soxhlet thimble in a flask containing boiling aqueous acetone. After extraction is complete, the purified product is filtered from the acetone solution. This method is rapid and requires only a small amount of acetone.

Purification by Acetone Extraction Using 20-50% Acetone:- Twenty-five grams of RDX (acidity, 0.12%) was placed in a Soxhlet thimble. This was suspended in a 1-l. round-bottomed flask directly below the lower end of the condenser so that it received the condensed acetone returning from the condenser while at the same time the product was kept hot by the hot vapors of the acetone. An RDX-saturated solution of 100 cc. of acetone and 100 cc. of water was

placed in the flask and heated under reflux on the steam bath. The extraction was complete in a short time. After refluxing for one hour, the mixture was filtered hot and washed with 50% acetone. Yield, 21 g.; acidity, 0.03%. The filtrate was used for another run.

Finer crystals were produced when 20% acetone was used. Even with this low concentration 25 g. of RDX was dissolved in less than one hour.

In these experiments an odor of formaldehyde was detected at the top of the condenser.

Properties of the Product

General properties

Melting points.- The RDX which was filtered from the reaction mixture at 60° (first crop) usually melted above 200°, corr., showing some softening below the melting point. The second crop melted lower (due to HMX present) and softened much more before melting. Total crop likewise showed a somewhat lower m. p.

The melting points were determined in an apparatus described by Hershberg (Ind. Eng. Chem., 8, 312 (1936)). We used dibutyl phthalate as the bath liquid. An Anschütz thermometer which was recently calibrated against a U. S. Bureau of Standards thermometer was employed. It was immersed in the bath to approximately the 195° mark. We have designated that temperature at which the first droplet of liquid can be seen as the beginning of the melting point. The final temperature recorded in the melting point signifies that the sample is completely melted.

Acidity, Vacuum Stability and Power.- As stated previously, the acidity of the products was brought to about 0.02% by acetone treatment (page 21). Prior to this treatment the acidity ranged from 0.1 to 0.3%.

We have little information on the vacuum stability of the product at 150°. However, material prepared at TEC, after acetone treatment, meets specifications in this respect.

Ballistic mortar tests carried out at Bruceton have shown that

The products possessed the power of British standard RDX. Some of the results are given in the following table:

Table VII

Ballistic Power of RDX Samples (TNT = 100)

Material	Ballistic Power
Standard RDX	150.0
H-1 First crop (filtered from reaction at 60°)	148.2
D-1 " " " " " "	149.5
H-2 Second crop (by diluting filtrate from H-1 to 30% acid and digesting for 3 hrs.)	149.5
H-3 Single crop (by treatment of the entire reaction as in H-2)	147.9
H-4 First crop material (H-1) heated in nitromethane solution with water on a steam bath for 3 hrs.; then the nitromethane distilled.	154.0
D-5 First crop (D-1) treated as in H-4	155.9

Note.- The H series were prepared from hexamine. The D series were prepared from hexamine dinitrate.

Sensitivity of RDX-HMX

Tests at Bruceton showed that first crop RDX (obtained by filtration of the reaction mixture at 60°) possessed normal sensitivity (i.e., the same sensitivity as British RDX prepared by direct nitration of hexamine) but second crops and single crops (obtained by drowning and simmering) prepared in the laboratory were usually abnormally sensitive.

Table VIII

SENSITIVITY OF RDX PRODUCTS

50% fire for 5 Kg. weight — Tests by Bruceton

British standard RDX 40-48 cm.

See Table VII for description of samples

Sample	Fall in cm. As received	Fall in cm. -100 +200
H-1 First crop	54	50
D-1 First crop	63	53
H-2 Second crop	10	7
H-3 Single crop	10	10
D-4 Single crop	10	14
H-4 First crop (Nitromethane-water)	68	43
D-5 First crop (Nitromethane-water)	80	56
D-5 First crop (Digested with 55 % nitric acid)	32	31

At about the same time, it was found at the Tennessee Eastman Corporation that certain sensitive needles had gradually deposited in drums of mother liquor, from pilot plant operations at the Western Cartridge Company, which had been diluted to 30% acetic acid and filtered. Similar sensitive needles had been isolated by TEC (Tennessee Eastman Corporation) from hot water which had been used to wash crude RDX product. We were requested to investigate this material in order to determine the cause of the high sensitivity, The nature of the needles, and the means of removing the material which caused the high sensitivity.

We had noticed previously that first crop RDX appeared as rhombs (looking superficially like cubes) while needles were present in the second crop to a considerable extent. It was found possible to convert pure RDX rhombs to needles by recrystallization from acetic acid or 70% nitric acid. If the needles were digested with 55% nitric acid (in a ratio of 1:5) on a steam bath for 12 hours, or were simply dissolved in nitromethane and the solvent removed by steam, the material was converted to rhombs. The pure RDX needles were no more sensitive than the rhombs. This showed that high sensitivity was not due simply to the fact that the material was in the form of needles.

Table IX

SENSITIVITY OF RDX NEEDLES AND RHOMBS

50% Fire for 5-Kg. weight. Tests by Bruceton

British Standard RDX 40-48 cm.

Sample	Treatment	Fall in cm. As obtained	-1004200
B-2	Needles obtained by recrystallization of 1st crop rhombs from AcOH	45	42
B-6	Rhombs obtained by treatment of 1st crop with nitromethane-water	36	38
B-5	Needles. B-6 recrystallized from AcOH	48	37

Examination showed that the sensitive products from the pilot plants were composed of RDX and HMX.

By recrystallization of 1.2 g. of the sensitive needles from acetone, a total of 0.93 g. of RDX (m.p. 200-202° corr.) was obtained. From the filtrate, after removal of the RDX from 5 g. of the needles, 0.4 g. (8%) of practically pure HMX was isolated.

Since no impurity other than HMX was isolated from the sensitive needles, it was decided to investigate the possibility that HMX itself in combination with RDX was responsible for the abnormal sensitivity. Experiment showed that such was the case, for a synthetic mixture of RDX (British) and HMX, which crystallized as needles from 30% acetic acid, proved to be abnormally sensitive (just as sensitive as the needles which had been sent us).

One g. of Woolwich process RDX and 0.1 g. of HMX were dissolved in glacial acetic acid and the hot solution was diluted with water to give a 30% acetic acid solution. The mixture was allowed to cool undisturbed. The product crystallized in long needles; m.p. 196-199° with previous softening. A determination of the sensitivity of this product at Bruceton showed that 50% of the samples fired with a 5 kg. weight dropping from a height of 6 cm. (standard RDX, 45 cm.)

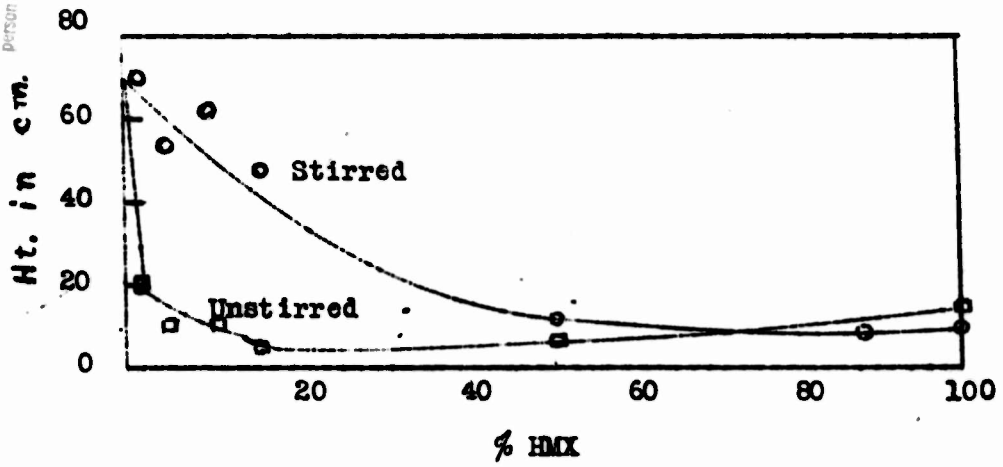
In further work it was found that RDX containing HMX was not always sensitive. In the pilot plant at TEC the product (which contains HMX) generally possessed normal sensitivity. Inasmuch as TEC stirred their batches, we investigated in the laboratory the effect of stirring on the sensitivity of the product. A number of mixtures of RDX and HMX were crystallized from 30% acetic acid both with and without stirring. The graph and accompanying table show the variation in the sensitivity of the samples with the concentration of HMX in stirred and unstirred mixtures.

Table X

All of the samples were made by dissolving the solids in hot glacial acetic acid, diluting with twice the volume of boiling water, and allowing to cool to room temperature with or without stirring. The stirred products consisted of stout crystals while the unstirred samples were obtained as needles or thin plates. Woolwich process RDX and pure HMX were employed in all of the samples.

% HMX	RDX g.	HMX g.	AcOH cc.	Yield Stirred	Yield Unstirred	Sensitivity Stirred	Sensitivity Unstirred
0	5	0	140		4.9	70 cm.	70 cm.
1	10	0.1	280	9.7	9.6	70	20
5	4.75	0.25	140	4.8	4.2	55	6
10	9.0	1.0	280	9.5	9.5	60 (12)	7
15	4.25	0.75	140	4.8	4.7	44 (18)	3
50	0.5	0.5	70	1.0	0.95	11	6
90	0.1	0.9	140	0.9	0.95	9	9
100	0	0.5	70	0.47	0.47	10	13

Notes: At times some samples have shown an anomalous change in sensitivity. Those values are given in parenthoses in the table. Other portions of the same samples later showed normal sensitivity. We are investigating the cause of this phenomenon.
The sensitivities were determined on one of our own impact machines on which Woolwich process RDX gave a value of 70 cm.



Examination of the table and graph shows that insensitive mixtures of RDX and HMX can be obtained containing up to 10-15% HMX when crystallized from 30% acetic acid with stirring during the cooling process. This is considerably more than the % HMX in the product made in the combination process. It is recommended that vigorous stirring be employed whenever RDX containing HMX is processed.

Sensitivity of Single Crop RDX (Contains HMX).- The application of the information gained from the experiments just described to actual reaction mixtures is shown in the following experiments.

Two normal runs were made (V-179 and V-180). Both of them were diluted at 65° with hot water to 30% acetic acid concentration and the mixture heated at 90-95° for two hours, one with stirring and the other without stirring. The first one was allowed to cool to room temperature with stirring, the other without stirring.

Run	Treatment	50% Fires
V-179	Single crop heated at 90-95° in diluted mother liquor for two hours with stirring; cooled with stirring over a five hour period	Above 55 cm.
V-180	Single crop heated at 90-95° in diluted mother liquor for two hours without stirring; cooled without stirring over a five hour period	21 cm.

This result shows that the mixture should be stirred vigorously during the simmering period and throughout the cooling operation.

Sensitivities of First Crop, Second Crop, and Single Crop Products After Various Treatments.- Digestion of first crop material with hot (90-95°) 30% acetic acid did not increase its sensitivity. Product of normal sensitivity was obtained by cooling the reaction mixture without dilution to 20° and filtering and also by diluting the reaction mixture with hot water and cooling. When the first of these was digested with hot water, it became sensitive. The data are given in Table XI.

Table XI

Tests by Bruceton

Sample	Treatment	Fall in cm. As obtained	Fall in cm. -100-200
C-1	First crop digested with hot 30% acetic acid	52	44
C-2	Reaction mixture (V-129) rapidly cooled to 20° without dilution and filtered.	48	44
C-3	Sample of C-2 digested with hot water (90-95°) for 24 hours.	15	19
C-4	Reaction mixture (V-168) diluted with hot water and cooled rapidly.	47	45

In Table XII is shown the sensitivity of second crop material

which had received treatments of various kinds. Most of the treatments failed to improve the product. Solution in nitromethane followed by steam distillation did improve the sensitivity. It is of interest that TEC have reported that analogous acetone purification (page 21) converted abnormally sensitive material to normally sensitive material.

Table XII

SENSITIVITY OF SECOND CROPS(RDX-HMX) Tests by Bruceton

Treatment	Fall in cm.	
	As received	Screened
Heated 90 minutes in acetic acid	16	12
From mother liquor that had been neutralized before diluting	5	6
Digested with 55% nitric acid	26	(erratic)14
Heated in diluted mother liquor 24 hrs.	6	6
Dissolved in nitromethane and steam distilled	30	23
From undiluted mother liquor	32	32

Sensitivity of HMX.- We prepared a batch of HMX from dinitropentamethylenetetramine according to Wright's method and recrystallized it first from acetone and then nitromethane. This HMX (m.p. 280-281°C, corr.) shot at 53 cm. on April 1, and at 43 and 47 cm. respectively on April 8 and April 9. A week after these results were obtained it was found that the HMX shot at 27 cm. We are at a loss to account for this change in sensitivity.

The following results were obtained when this same HMX was recrystallized from 30% acetic acid and acetone:

Sample	Height of fall in cm. of 5-kg. wt. for 50% fire.
HMX recrystallized from 30% acetic acid (small crystals)	27
HMX recrystallized from 30% acetic acid (large crystals)	17
HMX recrystallized from acetone	25

A second batch of HMX was prepared and purified in essentially the same manner as the first batch and melted at 270-280°, corr. This HMX (last crystallization from nitromethane) shot at 14 cm. When it was

recrystallized from 70% nitric acid, the needles of HMX which were obtained shot at 16 cm. When the needles were allowed to stand in the 70% nitric acid solution at room temperature for 24 hours, they changed to coarse granular (apparently bipyramidal) crystals which shot at 13 cm. Large crystals of this HMX prepared by slow cooling of a nitromethane solution shot at 25 cm.

COMPOSITION OF THE PRODUCT

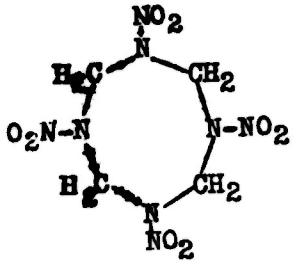
The product which is filtered off from the reaction mixture at 60° is practically pure RDX and probably contains no more than traces of HMX. Most of the HMX which is formed as a by-product remains in the filtrate, so that the second crop may contain an appreciable amount of this substance. In the single crop obtained by dilution of the entire reaction mixture with water, the amount of HMX amounts to 1-8% depending upon the procedure employed. Preliminary results indicate that a high yield product prepared in the pilot plant at the Tennessee Eastman Corporation (m.p. 191-194°) probably contains 5-8% of HMX.

Isolation of HMX.- One method of isolating HMX from second crop material consists in recrystallization from acetone.

Experimental.- Five grams of second crop material was dissolved in the minimum amount of boiling acetone. As soon as the solution had cooled to room temperature, the RDX was filtered by suction. Weight, 2.54 g., m.p. 200-202°. Some solid had precipitated in the filtrate during the filtration. When the filtrate was heated on the steam bath, some granular material did not dissolve. This was HMX; it was filtered from the hot solution; weight 0.2 g., m.p. ca.260°. An additional 0.2 g. of HMX was obtained from the acetone solution after it had stood overnight and was again warmed. Total yield, 0.4 g., (8%). After recrystallization from 70% nitric acid, it melted at 280°, (air bath). When mixed with authentic HMX, one sample melted at 285°, another at 273°.

Structure of HMX.- HMX has the same empirical formula as RDX. A molecular weight determination gave a value of 301 with an average deviation of 7. These facts together with its high melting point and stability led us to suggest the following structure for HMX and a possible mechanism of its formation:

This formula for HMX can also be written:



A molecular model of the proposed formula shows that the structure is strainless.

Anal. Calcd. for $CH_2N_2O_2$: C, 16.2; H, 2.73; N, 37.9
Found: C, 16.0; H, 2.68; N, 38.2.

Molecular Weight.- A sample of HMX supplied by Dr. G. F. Wright (his reference number 847 A), was used. The method employed was the boiling point elevation method of Menzies. Acetone was used as a solvent. The following values were obtained:
Mol. wt., 286, 312, 296, 301, 296, 302.
Average: 301. Average deviation: 7
Calculated for $C_4H_8N_8O_8$: 296. Dr. Wright obtained values in this region.

To check the method we made seven determinations on RDX.
Average mol. wt., 223 Average deviation, 9
Calculated for $C_3H_6N_6O_6$: 222.

Crystallographic Constants for HMX.- Three crystalline forms of HMX have been observed in our laboratory. They have been named (by Dr. J. R. Johnson) the alpha (rods), beta (bipyramids) and gamma forms.

The refractive indices are as follows:

Refractive Indices

Form	alpha	beta	gamma
Alpha	1.569-	1.569+	1.730
Beta	1.591	1.592	1.778
Gamma	- - -	1.580	1.667

The beta form appears to be the stable modification at room temperature.

Probable Absence of BSX

Inasmuch as BSX can be obtained from the same reagents used to prepare RDX by working at a lower temperature, the possibility that BSX might be present in the RDX was considered. A procedure was developed whereby it was possible to determine the presence of as little as 0.5% of BSX. This procedure was successfully applied to unknowns (synthetic mixtures containing RDX-HMX-BSX). When applied to two products produced at TEC (one of these was a high-yield product: 2.8 pounds of RDX from 1 pound of hexamine), no BSX was detected. There is nothing inconsistent with the view that TEC product consists of only RDX and HMX.

Procedure for Isolating BSX from a Mixture of RDX-HMX-BSX Containing 0.5 to 2% of BSX.- Five grams of the mixture is dissolved in 40 cc. of acetone in a 100-cc. wide-mouthed Erlenmeyer flask by heating on a steam bath. To the clear, hot solution is added 25 cc. of warm benzene and the mixture is heated on the steam bath in order to boil out the acetone and much of the benzene. When the precipitation of the solid takes place it is necessary to keep swirling the flask to prevent bumping. When the hot mixture is quite thick, it is removed from the bath and allowed to cool. The crystals are filtered off (this crop usually weighed 4.6-4.7 g.) and washed with some benzene. The filtrate and washings are now concentrated in a 50-cc. wide-mouthed Erlenmeyer flask on a steam bath a little beyond the point where crystallization sets in while hot. After cooling, the second crop of crystals (weight 0.25-0.30 g.) was filtered and washed with benzene. Concentration of the filtrate to a small volume (a few cc.) and cooling yielded the BSX (Note: Pure BSX melts at about 154°.

Results

No.	Mixture	Crop and M. p. 1st	2nd	3rd	4th
1.	4.5 g. RDX + 0.5 g. HMX + 0.10 g. BSX	4.02 g. 202-204°	0.84 g. 195->205°	0.12 g. 140-160°	

2.	TEC I-15-G (5 g.)	4.21 g. 202-204°	0.65 g. 193->205°	0.017 g. 185-190°	trace 194°
3.	TEC I-42-G (5 g.)	4.7 g. 197-201°	0.25 g. 192->205°	0.03 g. 192- 205°	
4.	TEC I-42-G (5 g.)	4.63 g. 201-203°	0.25 g. 190-197°	0.03 g. 190-200°	
5.	TEC I-42-G (5 g.) + BSX (0.100 g.)	4.61 g. 201-204°	0.28 g. 190->205	0.100 g. 145-155°	
6.	TEC I-42-G (5 g.) + BSX (0.025 g.)	4.72 g. 198-202°	0.23 g. 193->205°	0.03 g. 142-150°	

Note: No. 4 and 5 were given to the investigator as unknowns; to one of them had been added 0.100 g. of BSX, to the other none. The procedure then detected the presence of the BSX in the one containing it.

From the results it is apparent that as little as 0.5% (no. 6) of BSX can be detected. Both TEC I-15-G and TEC I-42-G showed no detectable amounts of BSX; even the last crop melted at a high temperature. We believe that even less than 0.5% can be detected by this procedure. At the present time there is nothing to indicate that the TEC pilot plant product is not simply RDX-HMX.

Investigation of the Roberts Method for the Determination of BSX. Inasmuch as no BSX was found in TEC product (RDX-HMX) by the direct isolation method, it seemed of interest to examine the procedure of Roberts and Watkins[2] which had been used by them and recently by Johnson for the estimation of BSX. In this procedure a sample is digested with nitric acid in order to eliminate the BSX. From the loss in weight a blank of 1% had to be subtracted which corresponded to the loss suffered when RDX was carried through the same process.

Apparently no blank had been determined for mixtures of RDX-HMX which was the material actually under consideration. Accordingly, we tested the procedure on the four materials below in order to determine if the presence of HMX altered the blank . Our procedure was essen-

tially the one used by Johnson (cf. Cornell University Progress Report, May 15-June 15, 1942) however we describe it here as we feel that the apparatus used, the times required and the phenomena observed are worth recording.

Experimental.- A weighed sample (approximately 10 g.) was dissolved in 70 cc. of 98% nitric acid in a one-liter wide-mouthed Erlenmeyer flask at room temperature; solution was rapidly effected and some brown fumes were evolved although the solution did not become hot. Forty-one cubic centimeters of water was added over a 15 minute period with cooling in an ice bath. Solid precipitated during the addition of water. The mixture was heated for 15 minutes with swirling in a water bath at 69-73° (many brown fumes were evolved; not all of the material went into solution in the hot). The flask was cooled under the water tap and 800 cc. of cold water was added dropwise over a 15 minute period while the flask was swirled and cooled in an ice bath. The flask was allowed to stand at room temperature for 20 hours and the solid was filtered off in a weighed Jena crucible and washed with 200 cc. of water. The material was oven-dried for 36 hours and weighed.

	Sample	Loss in Weight
1.	Woolwich RDX	2.15%
2.	Woolwich RDX	2.24
3.	Woolwich RDX 95%	3.47
	HMX (m. p. 281°) . . 5	
4.	Woolwich RDX 90	4.01
	HMX (m. p. 281°) . .10	

It is observed that our "blank" on Woolwich RDX was 2.1-2.2% (instead of 1%) and that with 5-10% HMX present the "blank" was 3.4-4.0%, considerably higher than for RDX alone. On the basis of these four experiments, one would have concluded that the RDX-HMX contained 1-2% of BSX in spite of the fact that no BSX was present. It is apparent that further work should be done before this procedure can be applied to the estimation of BSX.

RECOVERY OF REAGENTS

Recovery of Acetic Acid.- It is possible to recover nearly all of the acetic acid which is present in the reaction mixture. If the RDX has been filtered off at 60°, the filtrate is diluted to approximately 30% acetic acid with water and the mixture is heated on a steam bath under a reflux condenser (90-95°) for one to three hours. This digestion yields a better second crop and destroys a certain water insoluble oil which makes its appearance at the end of the vacuum distillation if this digestion is not employed. After the mixture has cooled to room temperature with efficient stirring the

second crop (nicely granular) is filtered from the mixture. A similar digestion at 90-95° is carried out if a single crop is isolated by diluting the entire reaction mixture with water to 30-50% acetic acid concentration; slow cooling with vigorous agitation is employed in order to avoid the formation of abnormally sensitive product.

The nitric acid in the filtrate is neutralized by means of ammonium hydroxide (thymolsulfonephthalein used as indicator) and the dilute acetic acid is distilled from the mixture under reduced pressure (15 mm.) at 45-60° (flask in a water bath). About 88-93% of the total acetic acid is present in the distillate, which is suitable for concentration to glacial acetic acid. It is not certain whether complete evaporation of the dilute acetic acid is a safe operation on a large scale, and in practice up to now some acetic acid is allowed to remain in the sludge.

Recovery of Ammonium Nitrate.- The residue, which remains after the removal of the dilute acetic acid, was dissolved in a small amount of water and the solution filtered from a small amount (about 0.2 g.) of insoluble solid. The solution was evaporated to dryness (treatment with Norit is beneficial in removing color), the residue is moistened with glacial acetic acid and the solid ammonium nitrate is filtered, washed with a little acetic acid and dried. The ammonium nitrate is pure white, melts at 164-166° and was found to be satisfactory for preparing RDX. Its weight corresponds to about 30-50% of the amount originally used in the preparation of the RDX.

FLOW SHEET FOR THE RECOVERY OF ACETIC ACID AND AMMONIUM NITRATE

Reaction mixture

Filter off 75-80 g. RDX at 60° (m.p. 200-203°)

Dilute filtrate to 30% acetic acid and digest at 90-95° for at least one hour* Let cool with vigorous stirring. Filter

Dilute entire reaction mixture to 30% acetic acid and digest at 90-95° for at least one hour. Let cool with vigorous stirring. Filter.

Second crop 10-13 g. M.p. 191-3°

Nitric acid in filtrate neutralized with ammonium hydroxide. Acetic acid distilled at 45-60° at 15 mm.

Single crop 85-90 g. M.p. 195-200°

Dilute acetic acid 88-93% of the total acetic acid.

Residue. Addition of 20 cc. of water gives a clear aqueous solution (no oil) and about 0.2 g. of RDX (m.p. ca. 190°). Filter and evaporate to dryness

Yellow residue (26-27 g.) Break up lumps, digest with 13 cc. of cold glacial acetic acid, filter, wash with acetic acid.

Perfectly colorless ammonium nitrate. Yield, 19.5 g. (m.p. 164-166°)

* Longer heating (4-6 hours) gives somewhat better crystals.

STUDIES ON BSX

Preparation of BSX.- In the previous report the preparation of BSX was described. It was obtained by allowing acetic anhydride, 98% nitric acid, ammonium nitrate and hexamine dinitrate to react in the cold (rather than at 75° when RDX is formed). BSX can be prepared under the same conditions without the use of ammonium nitrate.

Experimental.- To an ice-cold mixture of 60 cc. of acetic anhydride and 13.8 cc. of 98% nitric acid there was added with stirring 20.8 g. of hexamine dinitrate. Not much heat was evolved and the solid could be added in less than five minutes. The mixture was warmed slowly in the course of one-half hour to 75° with stirring and held there for five minutes (a few brown fumes). The slow addition of 160 cc. of water precipitated 23.3 g. of product.

A 15 g. portion of the crude product was dissolved in 100 cc. of acetone, the solution was treated with Norit and Filter-Cel and the acetone was removed partially by distillation. When the volume had reached about 25 cc., an equal volume of ethyl acetate was added and the mixture evaporated to incipient crystallization, seeded with BSX and allowed to cool. The product was filtered and washed with ethyl acetate; weight, 7.6 g.; m.p. 153-154°.

A portion (5 g.) of the crude product was heated for 24 hours on a steam bath in 40 cc. of 70% acetic acid. This treatment destroyed the BSX and other low-melting compounds. Upon evaporation of the aqueous acetic acid solution, 0.35 g. of RDX (m.p. 201-204°) was obtained. This indicates that the crude product contains about 7% of RDX.

Molecular Weight of BSX.- Bachmann and Sheehan (August 1941) in preliminary work on the molecular weight of BSX using the apparatus of Menzies with acetone as the solvent obtained a value of about 350. This meant that the structure, diacetylmethylenedinitramine, which had been tentatively suggested on the basis of analytical values alone, had to be abandoned. British workers have reported the values: 416 (boiling point method in acetone); 346 (freezing point depression in TNT); 316 (Rast method); 353 ± 2 (X-ray method). We have now repeated our original work and have obtained the following two sets of values: 323,320,328,344,350 (average, 332) and 335,350,342,341 (average 342).

Degradation Experiments.- Roberts and Watkins hydrolyzed many samples of BSX and titrated the acid formed. They calculated the analysis as acetic acid but reported only two tests which identified the titrated acidity as acetic acid (the calcium acetate-indigo color test and the formation of ethyl acetate which was detected by its odor). We have identified the acid liberated on hydrolysis in various ways in order to eliminate the possibility that the acetic acid was present only as a contaminant. A sample of BSX was hydrolyzed with hot syrupy phosphoric acid, the volatile acid was distilled, the distillate was neutralized and evaporated in order to remove formaldehyde. Oxidizable acid (formic acid) was destroyed by potassium permanganate and the purified acid was converted to its sodium salt (sodium acetate). The following methods of identification were employed:

1) Determination of the Duclaux numbers.
2) Cacodyl test with arsenious acid.
3) Formation of ethyl acetate.
4) Test with Lanthanum nitrate, iodine and ammonium.
5) Conversion to anhydrous acid by distillation of a mixture of the sodium salt and concentrated sulfuric acid. The liquid acid had a b.p. of about 110° and m.p. 10°.

6) Conversion to the silver salt. A 0.2117 g. sample yielded 0.1368 g. of silver on ignition. Calcd. for $AgC_2H_3O_2$: Ag, 64.65%. Found: 64.62%.
7) Preparation of the solid p-bromphenacyl derivative. Identified as p-bromphenacyl acetate by melting point and mixed melting point.

Hydrolysis:- Ten grams (0.28 moles) of pure BSX (m.p. 154.5-155.5°, corr.) was warmed on a steam bath under reflux condenser with 100 cc. of syrupy orthophosphoric acid (85%). A clear solution was obtained after 30 minutes. At the end of 24 hours paraformaldehyde had condensed in the condenser. One hundred cubic centimeters of water was added and the solution was distilled slowly using a Kjeldahl bulb to trap spray. Two separate portions of water were added and the distillation was repeated twice. Volatile acid, formaldehyde and water comprised the distillate. Titration of the three fractions obtained showed a total of 0.060 moles of acid. A portion of the distillate was made alkaline with sodium carbonate and titrated with permanganate. The reducing substance, calculated as formaldehyde, corresponded to a total of 0.099 moles (calcd. for four methylene groups: 0.112 moles). After filtering the manganese dioxide, the aliquot was returned to the main body of the sample and the whole evaporated to dryness. The residue was dissolved in water and all oxidizable substances destroyed by permanganate. The manganese dioxide was filtered off and the filtrate evaporated to dryness. The residue was dissolved in about 100 cc. of water and treated with an excess of syrupy phosphoric acid. The solution was distilled, and when the distillation had ceased, 50 cc. of water was added and the distillation repeated. The total distillate had a volume of about 150 cc. and contained 0.055 moles of acid (calcd. for two acetyl groups: 0.056 moles).

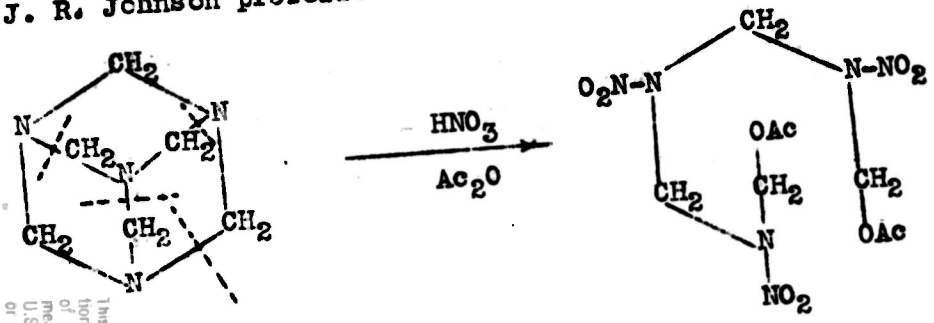
This solution was used for determining the Duclaux numbers and then all of the solution was neutralized and evaporated to dryness. The sodium acetate thus obtained was used for the several tests mentioned in the discussion. In addition a search was conducted for other acids. Phosphate, nitrate, and halide were found to be absent.

Structure of BSX.- Considerable work has been done by the British[2] on the structure of BSX. They have concluded: (1) its molecular formula is $C_8H_{14}N_6O_{10}$; (2) that all of its nitrogen is in nitramino groups; and that (3) upon hydrolysis it yields four moles of formaldehyde and two moles of acetic acid. They also proposed a structural formula and a possible mechanism for its formation.

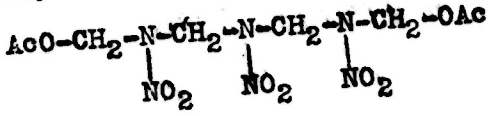
Our molecular weight values are in accord with the molecular weight required for their proposed formula. We have proved conclu-

sively that the volatile acid formed on the hydrolysis of BSX is acetic acid; and that two moles come from one mole of BSX. The formaldehyde evolved corresponds approximately to the presence of four methylene groups in BSX.

The formation of a likely compound possessing the requisite molecular formula and properties is shown in the following scheme. This involves merely the scission of four bonds of the hexamine molecule and does not necessitate the recombination of fragments. The structure of the resulting compound is one of the two that Dr. J. R. Johnson preferred to the structure proposed by Roberts.



This formula may also be written:



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1. Bachmann, "The Preparation of Cyclonite (RDX)", Final Formal Report, September 20, 1941.

2. Roberts and Watkins, British Report, WA-98-21, April, 1942.

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ABSTRACT:

The principles and conditions were determined for obtaining RDX (or RDX-HMX) in high quality and in excellent yield. The RDX was prepared by the action of nitric acid, acetic anhydride, and ammonium nitrate on hexamine which was added in the solid form, in the form of dinitrate, and also in acetic acid. The processing of the product is described. Nearly pure RDX can be filtered directly from the reaction mixture, or a mixture of RDX-HMX can be obtained by diluting the reaction mixture with water. An acetone and a nitromethane purification of the product were worked out which gave a product with an acidity, vacuum stability, and ballistic power within the specifications. The effect of various factors on the sensitivity of RDX-HMX mixtures is discussed. A structure is proposed for the high-melting impurity, HMX, which accompanies the RDX. Some work is reported on the study of BSX, a substance which can be obtained from the same reagents used to prepare RDX.

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