QUARTERLY PROGRESS REPORT

DEVELOPMENT DIVISION

APRIL - JUNE 1976

For
Lawrence Livermore Laboratory
Livermore, California

MASTER

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THERMAL PROPERTIES

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DEVELOPMENT DIVISION

April - June 1976
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ABSTRACT

PETN thermal decomposition studies were continued at 353 and 333 K. The 353 and 333 K results indicate very long induction periods compared to decomposition at 373 and 383 K.

The source of some of the variations in the chemical reactivity test data is due to variations in the helium line pressure. Data were obtained for PBX 9404 using methane as an internal standard. The use of an internal standard did not reduce the variation during any given day but it did reduce the day-to-day variations. Using a mixture of nitrogen and nitrous oxide it was determined that the precision of the instrument and integrator are about 1%.

DTA and chemical reactivity results at 393 and 423 K are reported for RX-03-BB with two epoxy samples provided by LLL. The DTA thermograms indicate that the epoxies are reactive with RX-03-BB above 523 K, and the chemical reactivity data indicate a slight reaction between the RX-03-BB and both epoxy samples.

Heat-of-fusion measurements were made for a PETN control sample (Lot No. 1072-426-12) and compared with measurements made on the same lot during the past four years. There is no indication that the apparent heat-of-fusion is changing with time.

DISCUSSION

THERMAL DECOMPOSITION OF PETN

The gas evolution analyses of PETN samples sealed in glass vials has continued. A complete series of analyses were made on PETN samples conditioned at 383 K, and several analyses were made on PETN samples conditioned at 353 and 333 K. The analyses of the atmosphere in all of the samples taken to date are given in Table I and a graph of these data are shown in Fig. 1. As the 373 K samples approached 1.6% decomposition, the rate decreases. However, this was not observed at 383 K. These data indicate that the 353 and 333 K samples have very long induction periods.

No attempt has been made to calculate the reaction rate because of the very limited amount of data at 353 and 333 K.

Last quarter it was reported that the ratio of CO to NO varied with different PETN samples. This was investigated this quarter and the results indicate that the ratio is dependent on the sample holder material. Table II gives data from six samples of PETN conditioned in different atmospheres for 43 days at 373 K in stainless steel sample holders. The ratio of CO to NO is approximately unity, except for the two samples which leaked. This is the same lot of PETN used in the decomposition investigation in glass sample holders and the CO to NO ratio in that case was approximately 5 to 1.

Table I. Gas Analysis for 0.50 g PETN Samples Conditioned
in a Helium Atmosphere at Selected Temperatures

(Gas Volumes in ml and Corrected to STP).

<u>Days</u>	<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>	<u>Fraction Decomposed^a x 10³</u>
<u>Samples Conditioned at 383 K</u>							
2	0.059	0.047	0.0004	0.054	0.027	0.187	0.93
6	0.149	0.168	0.040	0.310	0.121	0.788	3.94
9	0.492	0.492	0.088	1.144	0.355	2.571	12.86
13	0.875	0.736	0.094	2.047	0.563	4.315	21.76
<u>Samples Conditioned at 373 K</u>							
9	0.060	0.067	0.008	0.105	0.043	0.283	1.41
15	0.118	0.135	0.033	0.265	0.095	0.645	3.23
22	0.212	0.189	0.031	0.524	0.150	1.108	5.54
22	0.227	0.210	0.043	0.497	0.146	1.123	5.62
32	0.277	0.218	0.043	0.665	0.175	1.378	6.89
42	0.372	0.273	0.040	0.809	0.219	1.713	8.57
53	0.490	0.335	0.051	1.186	0.216	2.327	11.64
59	0.583	0.355	0.045	1.432	0.340	2.755	13.78
66	0.623	0.358	0.043	1.552	0.364	2.940	14.70
74	0.729	0.395	0.027	1.636	0.379	3.166	15.83
99	0.670	0.373	0.038	1.741	0.399	3.220	16.10
<u>Samples Conditioned at 353 K</u>							
22	0.004	0.019	0.016	0.005	0.002	0.046	0.23
58	0.015	0.004	-0-	0.007	0.002	0.028	0.14
60	0.044	0.018	-0-	0.013	0.003	0.078	0.39
102	0.016	0.012	-0-	0.04	0.004	0.045	0.23
162	0.023	0.015	-0-	0.025	0.008	0.071	0.36
196	0.025	0.027	0.004	0.032	0.011	0.098	0.49
<u>Samples Conditioned at 333 K</u>							
58	0.005	0.027	0.023	0.007	0.001	0.063	0.31
140	0.009	0.002	-0-	0.002	-0-	0.014	0.07
196	0.002	0.001	-0-	0.001	0.012	0.016	0.08

^aTotal gases evolved/2 x 10²

Fig. 1. Fraction Amount of Decomposition for PETN at 383, 373, 353, and 333 K as a Function of Time

Table II. Atmosphere Analysis for 0.50 cm PETN Samples
Conditioned at 373 K for 43 Days
(Gas Volumes in mL Corrected to STP)

<u>Initial Atmosphere</u>	<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>	<u>Comments</u>
Vacuum	0.325	0.220	0.210	0.819	0.192	1.766	Small air leak
	0.193	0.398	0.258	1.528	0.311	4.422	
40 cm He	0.503	0.352	0.290	1.244	0.297	2.686	
	0.554	0.369	0.396	1.480	0.331	3.130	
67 cm He	0.848	0.375	0.287	1.367	0.314	3.191	Very small air leak
	0.411	0.289	0.211	0.993	0.244	2.148	

VARIATIONS IN THE CHEMICAL REACTIVITY TEST DATA

It was reported last quarter that a system had been designed such that an internal standard could be run with each chemical reactivity sample. Tests have been made for PBX 9404 using methane as the internal standard, and during these runs it was determined that some of the variations in the data were caused by variation in the helium line pressure. Previously data indicated that small changes in line pressure had little or no effect. It was determined that several hours are required for the instrument to stabilize from a change in the line pressure, so tests made from one to two hours after the line pressure changed would show little effect. For the test results given in Table III a 34 kPa change in the helium line pressure causes a 0.067 mL change in the total volume of gas evolved from PBX 9404. Using methane to normalize the data, the change was reduced to 0.031 mL. However, the methane normalization did not reduce the variations of the total volume of gas evolved by PBX 9404 during a given day.

An inline regulator was added to the chemical reactivity test apparatus, recalibrated, and a second series of runs was made on PBX 9404, again using methane for an internal standard. These results are given in Table IV. An internal standard did not reduce the relative standard deviation for the total gas evolved, but the inline regulator did reduce the day-to-day variation in the total volume of gas evolved. The mean and standard deviation for all the runs over a 4 day period were $0.433 \text{ mL} \pm 17$ and $0.417 \text{ mL} \pm 16$ for the total and normalized total, respectively.

The reproducibility or precision of the chemical reactivity system was evaluated with tests using a mixture of nitrogen and nitrous oxide. These data are given in Table V. The ratio of the nitrogen to nitrous oxide should be a constant, since the same amount of gas was used for each run. The mean, standard deviation and relative standard deviations were calculated for each, and the data indicate that the precision of the instrument is about 1%. This includes errors in the gas chromatograph and the integrator.

Additional tests are planned to determine if the precision of the system can be improved.

REACTIVITY OF RX-03-BB WITH TWO EPOXY SAMPLES

A request was received the latter part of this quarter to evaluate the reactivity of RX-03-BB with two epoxy samples. A complete series of tests is planned but has not been completed. However, the available data are given to provide preliminary information for the reactivity of RX-03-BB with the two epoxy samples.

Table III. Chemical Reactivity Test Data for PBX 9404
(Gas Volumes in ml Corrected to STP)

	<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>	<u>Methane c/μl</u>	<u>Normalized Total^a</u>
Helium Pressure	0.031	0.036	0.196	0.130	0.016	0.409	105.5	0.399
448 kPa	0.027	0.036	0.205	0.127	0.016	0.411	108.5	0.390
	0.023	0.038	0.206	0.137	0.018	0.422	107.0	0.406
	0.024	0.038	0.213	0.131	0.016	0.422	106.7	0.407
	0.021	0.037	0.210	0.126	0.016	0.410	110.7	0.381
Mean						0.415		0.397
σ						0.006		0.011
Relative σ						1.5%		2.8%
Helium Pressure	0.025	0.043	0.228	0.146	0.018	0.460	114.5	0.414
414 kPa	0.027	0.044	0.229	0.149	0.020	0.469	116.0	0.416
	0.024	0.045	0.249	0.161	0.021	0.500	117.2	0.439
	0.023	0.045	0.250	0.159	0.020	0.497	115.8	0.442
Mean						0.482		0.428
σ						0.020		0.015
Relative σ						4.0%		3.4%

^aNormalized to 102.9 counts/μl of methane

Table IV. Chemical Reactivity Test Data for PBX 9404
(Gas Volumes in ml and Corrected to STP)

	<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>	<u>Methane c/μl</u>	<u>Normalized Total</u>
Runs normalized to 95.63 c/μl	0.029	0.039	0.202	0.134	0.016	0.420	95.72	0.420
	0.025	0.039	0.219	0.141	0.017	0.411	97.73	0.432
	0.014	0.039	0.226	0.147	0.018	0.444	96.95	0.438
	0.022	0.041	0.229	0.152	0.019	0.463	98.47	0.450
	0.021	0.040	0.221	0.138	0.017	0.439	99.20	0.421
Mean						0.441		0.432
σ						0.015		0.012
Relative σ						3.4%		2.8%
Runs normalized to 93.70 c/	0.025	0.038	0.209	0.132	0.016	0.420	96.23	0.409
	0.021	0.038	0.217	0.148	0.018	0.442	95.34	0.434
	0.024	0.040	0.213	0.136	0.016	0.429	97.14	0.414
	0.023	0.041	0.219	0.141	0.017	0.441	97.30	0.425
	0.020	0.040	0.213	0.143	0.018	0.434	97.48	0.417
Mean						0.433		0.420
σ						0.009		0.010
Relative σ						2.1%		2.3%
	0.030	0.036	0.194	0.133	0.018	0.411	95.33	0.404
	0.021	0.035	0.191	0.124	0.016	0.387	97.07	0.374
	0.020	0.038	0.208	0.143	0.019	0.428	96.85	0.414
	0.023	0.039	0.211	0.143	0.019	0.435	98.18	0.415
	0.022	0.040	0.203	0.136	0.017	0.418	98.19	0.398
Mean						0.416		0.401
σ						0.019		0.017
Relative σ						4.5%		4.2%
	0.030	0.038	0.202	0.137	0.017	0.424	96.83	0.410
	0.030	0.040	0.209	0.146	0.018	0.443	99.44	0.417
	0.022	0.038	0.216	0.152	0.019	0.447	98.57	0.424
	0.028	0.041	0.213	0.145	0.018	0.445	99.96	0.417
	0.023	0.040	0.223	0.144	0.017	0.447	101.05	0.414
Mean						0.441		0.416
σ						0.010		0.005
Relative σ						2.3%		1.2%
Total Mean						0.433		0.417
σ						0.17		0.16
Relative σ						3.9%		3.8%

Table V. Repeated Analysis of a Mixture of Hydrogen and Nitrous Oxide
(Integrator Counts)

	<u>N₂</u>	<u>N₂O</u>	<u>Ratio of N₂/N₂O</u>
	4093	1923	2.128
	4086	1901	2.149
	4094	1909	2.145
	4116	1875	2.195
	4125	1911	2.159
	4160	1936	2.149
	4143	1935	2.141
	4131	1909	2.164
Mean	4118	1912	2.154
σ	26	20	0.020
Relative σ	0.6%	1.0%	0.9%

The DTA thermograms of RX-03-BB and the two epoxy samples are shown in Figs. 2 and 3. On comparing the thermograms it is apparent that the mixtures have a small broad exotherm between 525 and 600 K and there is no exotherm present in the thermograms of the individual components. This indicates that the materials are reactive in this temperature range and could be reactive at lower temperatures.

Chemical reactivity test results for samples conditioned at 393 and 423 K are given in Table VI.

The 423 K data do not show an excessive amount of gas evolved by the mixtures, but their chromatograms do show differences. There is concern as to what these differences indicate. Figs. 4 and 5 show the chromatograms of RX-03-BB with Epoxy ABV-23 conditioned at 393 and 423 K, respectively. The mixture conditioned at 423 K shows methane, an unidentified peak between CO_2 and N_2O , a peak between N_2O and water, and the water peak has another peak superimposed on it which is probably ammonia^a. The sample was discolored after conditioning at 393 and 423 K.

The chemical reactivity test data show some reactivity between RX-03-BB and both epoxies, but if these data are judged on the same basis as other explosives (HMX, RDX, PETN, etc.), the epoxy samples would not be considered reactive. However, since TATB is a new and different type of explosive and there are no baseline data for comparison this degree of reactivity should probably be considered significant. Until more information is obtained about the reactivity of these materials RX-03-BB should not be stored in contact with the epoxies for more than six months.

To obtain baseline data for RX-03-BB, a coupon test assembly will be thermally aged to investigate the reactivity of RX-03-BB with one of the epoxy samples.

HEAT OF FUSION OF PETN

The requirement for the heat-of-fusion measurement on all lots of LX-13 grade PETN was discontinued during the latter part of 1974. However, the measurements are still being made on the PETN control sample (Lot 1072-426-12) to determine if the apparent heat of fusion changes with time. The data on the control lot are given in Table VII and there has been no measurable change in the four years.

^aLast quarter two adhesives tested with RX-03-BB gave a similar shaped peak which was identified as water and ammonia by mass spectrometry.

Fig. 2. DTA Thermograms of RX-03-BB, ABV-23 Epoxy and a Mixture of the Two (Heating Rate 11 K/min)

Fig. 3. DTA Thermograms of RX-03-BB ABV-24 Epoxy and a Mixture of the Two (Heating Rate 11 K/min)

Table VI. Chemical Reactivity Test Data for RX-03-BB
with two Epoxy Formulations

(Gas Volumes in ml Corrected to STP)

	Temp (K)	Sample Wt (g)	N	CO	NO	CO ₂	N ₂ O	Total	Comments
RX-03-BB	393	0.250	0.009	-0-	-0-	0.002	-0-	0.011	
	393	0.250	0.009	-0-	-0-	0.002	-0-	0.011	
ABV-23	393	0.250	0.010	-0-	-0-	0.031	-0-	0.041	
	393	0.250	0.007	-0-	-0-	0.036	-0-	0.043	
ABV-24	393	0.250	0.008	-0-	-0-	0.020	-0-	0.028	
	393	0.250	0.015	-0-	-0-	0.020	-0-	0.035	
RX-03-BB with ABV-23	393	0.250/0.250	0.014	T	-0-	0.033	T	0.047	Peak not resolved from CO ₂
	393	0.250/0.250	0.014	T	-0-	0.034	T	0.048	
RX-03-BB with ABV-24	393	0.250/0.250	0.010	-0-	-0-	0.027	T	0.037	
	393	0.250/0.250	0.008	-0-	-0-	0.027	T	0.035	
RX-03-BB	423	0.250	0.027	T	-0-	0.005	T	0.032	
	423	0.250	0.011	T	-0-	0.006	T	0.017	
ABV-23	423	0.250	0.025	-0-	-0-	0.050	-0-	0.075	
	423	0.250	0.008	-0-	-0-	0.052	-0-	0.060	
ABV-24	423	0.250	0.024	T	-0-	0.028	-0-	0.052	
	423	0.250	0.021	T	-0-	0.027	-0-	0.048	
RX-03-BB with ABV-23	423	0.250/0.250	0.026	0.002	-0-	0.069 ^a		0.097	
	423	0.250/0.250	0.023	0.002	-0-	0.079 ^a		0.104	
RX-03-BB with ABV-24	423	0.250/0.250	0.006	0.001	-0-	0.044 ^a		0.051	
	423	0.250/0.250	0.017	0.001	-0-	0.016 ^a		0.034	

^aMultiple peaks with CO₂ and N₂O trace of CH₄, small peak before H₂O, peak with H₂O sample turn medium brown

Fig. 4. Chemical Reactivity Test Chromatogram of RX-03-BB with ABV-23 Epoxy Conditions at 393 K

Fig. 5. Chemical Reactivity Test Chromatogram of RX-03-BB with ABV-23 Epoxy Conditioned at 423K

Table VII. Heat-of-Fusion of the PETN Control
(Sample Lot 1072-426-12)

<u>Date</u>	<u>ΔH_f (J/kg x 2.39×10^{-4})^a</u>	<u>Standard Deviation (J/kg x 2.39×10^{-4})^a</u>
7-19-73	34.87	0.10
7-29-72	34.95	0.06
2-07-73	34.86	0.17
5-11-73	35.08	0.11
2-06-74	35.07	0.14
4-27-74	35.07	0.10
6-06-74	35.21	0.09
7-17-74	35.53	0.20
10-29-74	35.00	0.12
12-26-74	35.00	0.23
5-19-76	35.00	0.15

MEAN (35.06)

σ 0.18

^a(1 cal/g = J/kg x 2.39×10^{-4})

FUTURE WORK, COMMENTS, CONCLUSIONS

The thermal decomposition investigation of PETN was continued and samples conditioned at 383 K were analyzed this quarter. Comparison of the data from PETN samples conditioned at 383, 373, 353 and 333 K show that the 353 and 333 K samples have a long induction period, and after 200 days very little decomposition has occurred. The 373 K sample showed a decrease in the rate of decomposition as the amount of decomposition reaches 1.6%.

The ratio of CO to NO evolved from PETN is dependent on the sample holder material. If all glass sample holders are used the ratio of CO to NO is large (approximately 5) and if the sample is sealed in a stainless steel sample holder the ratio approaches unity.

Part of the variation in the Development Division's chemical reactivity test apparatus has been due to changes in the helium line pressure. This has been corrected by installing an inline regulator and the day-to-day variations have been significantly reduced.

The use of an internal standard for the chemical reactivity test apparatus has not reduced the data variations on a given day but it has helped to reduce day-to-day variations.

The precision of the chemical reactivity apparatus and integrator was determined to be about 1%. Work will continue toward the improvement of the precision.

Preliminary data were obtained for the reactivity of RX-03-BB with two epoxy samples requested by LLL. The results show some reactivity of the materials with RX-03-BB. If this degree of reactivity were observed with explosives such as HMX, RDX and PETN, the epoxy samples would be considered nonreactive, but without baseline data for RX-03-BB the epoxy samples should be considered moderately reactive and should not be stored in contact with RX-03-BB for periods greater than six months.

The apparent heat-of-fusion of PETN is dependent on the recrystallization method. If PETN is crash precipitated, the heat-of-fusion is less than samples prepared by slow evaporation of the solvent. The heat-of-fusion measurements during the past four years indicate no change in the heat-of-fusion of PETN control Lot 1072-426-12.

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