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THERMAL PROPERTIES & CHEMICAL REACTIVITY

SANL 712-005

L. C. Myers

October, November, December 1969

DEVELOPMENT DIVISION

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This project is to determine the thermal and chemical reactivity properties of explosives, and to continue the development and evaluation of useful thermal tests.

ABSTRACT

The impurities in FEFO and relatively pure FEFO fractions are being obtained by preparative gas chromatography. The use of gas chromatography-mass spectrometry to identify the impurities in FEFO was not successful.

Gas chromatography analysis of gas samples taken from the coupon test are reported.

The analysis from the third compression type coupon test is reported. The LX-09 lost some of its mechanical strength and was a dark purple.

Some of the problems of measuring sample temperature in the high pressure DTA are discussed. DTA thermograms at ambient and elevated pressures are reported for FEFO, nitromethane, $\text{Na}_3\text{PO}_4 \cdot 10 \text{H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$.

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DISCUSSIONThermal Decomposition Studies on FEFO

The small Beckman Model GC-2A gas chromatograph equipped with 5/8-inch diameter column is being used to purify FEFO and to concentrate its low boiling impurities. With the large column the peaks are broad but analysis of the samples using an analytical column (1/8-inch x 1 meter with OV3 on chromosorb WHP) in the Hewlett Packard Model 5700 gas chromatograph shows a concentration of the impurities in one fraction and the FEFO fraction contains a very small percentage of impurities.

Attempts to analyze the impurities with the TOF mass spectrometer connected directly to the 5700 GC were not successful. With the connecting line at 150 to 175°C the system could not be adequately cleaned up between peaks; therefore, meaningful results could not be obtained from the spectra. Higher line temperatures were not tried because of the possibility of decomposing the sample before it reached the mass spectrometer.

A sampling system has been designed and is being assembled to study the isothermal decomposition products of FEFO as a function of time. This system will allow a small gas sample (~ 7 cc) to be taken and analyzed by both GC and mass spectrometry. The analysis by gas chromatography will give better results on small quantities of gas than the mass spectrometer. The mass spectrometer will be used as a check to determine if every component is being accounted for.

Coupon Testing

A system is now in operation to take small gas samples from the coupon test container for analysis by either gas chromatography (GC) or mass spectrometry (MS).

A summary of the first series of gas analysis by GC is given in Table I.

The analysis of the third compression type coupon test sample (No. 16) has been completed. This assembly was stored at 80°C for 9 months. An explanation of the compression type test assemblies was reported in the last quarterly report.

The observations made when disassembling this container were:

1. The PAM 28 was tacky, indicating some reversion had occurred.
2. The boron pad appeared to have lost some of its strength.
3. The LX-09 was much darker purple than the control. Its mechanical strength changed: it was softer and more flexible.

Shore type D durometer readings were taken to give some indication as to the change in the mechanical strength of the LX-09. A control sample had a reading of 70 @ 15 sec, while test sample No. 16 had a reading of 60 @ 15 sec.

The color change observed with sample No. 16 was different from that observed with sample No. 12 aged 5 months at 80°C, being a dark purple versus the tan of sample No. 12. See photographs of the controls and sample Nos. 12 and 16 in Fig. 1.

Table I

Gas Analysis of Atmosphere in Coupon Test Assemblies
Aged ~ 265 Days @ 80°C

<u>Material</u>	<u>Container No.</u>	<u>N₂</u>	<u>O₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>
LX-09/PAM 28/Mulberry	25	4.5	Trace	0.92	0.2	3.89	4.27
LX-10/PAM 28/Mulberry	24	0.88	0.17	-	-	0.19	2.04
LX-09/Sylgard/Mulberry	27	4.1	1.0	0.3	-	2.2	2.5
LX-10/Sylgard/Mulberry	26	0.98	0.19	-	-	0.07	1.55

Sample No. 12
Opposite the Mulberry

Control

Sample No. 12
Facing the Mulberry

Control Samples (light purple)

Sample No. 16 (dark purple)

Fig. 1
LX-09 from Sample Nos. 12 and 16

There were no noticeable differences in the DTA, pyrolysis, and TGA thermograms of the control sample and sample No. 16.

The Henkin's time-to-explosion (TE) for sample No. 16 and a control are given in Table II and a plot of the data is shown in Fig. 2. The differences in the TE between the control and sample No. 16 are not as great as reported with sample Nos. 10 and 12. These data suggest that those samples which fade will have shorter TE than those which become darker.

Table II

Time-to-Explosion
(seconds)

<u>Lot Number</u>	<u>Temperature, °C</u>			
	<u>222</u>	<u>229</u>	<u>234</u>	<u>240</u>
Std 94-1	647	531	320	121
	692	489	320	123
	682	482	308	132
		500	286	105
Harmonic mean	(673)	(500)	(308)	(119)
TS No. 16	663	443	253	84
	894	426	309	79
	869	448	259	62
		*		70
Harmonic mean	(794)	(439)	(271)	(70)

**No explosion*

Fig. 2

F-8

Time-to-Explosion
LX-09 Coupon Samples

High Pressure DTA

The previous quarter was spent getting the high pressure DTA equipment to operate at as high a pressure and temperature as possible. The present upper limits are $\sim 250^{\circ}\text{C}$ at 10,000 psi when heated at a rate of $10^{\circ}\text{C}/\text{min}$.

A heating jacket has been ordered for the reaction vessel, which houses the DTA cell, to extend the upper temperature and pressure limits.

The accuracy of the sample temperature measurement was investigated. The DTA cell used in the preliminary investigation was an aluminum cylinder with three sample wells: one for the test sample and two for reference samples. The differential temperature was obtained between the test sample and one reference sample. The sample temperature was obtained from the second reference sample.

Thermograms of indium showed a decrease of $\sim 12^{\circ}\text{C}$ in the melting point as the pressure varied from ambient to 10,000 psi. Bundy¹ showed that high pressures will change the thermocouple EMF but the change for Chromel-Alumel thermocouples would be less than 0.5°C at 10,000 psi. Babb² showed that the melting point of indium should be increased by $\sim 3^{\circ}\text{C}$ at 10,000 psi.

¹Bundy, F.P., *J. Appl. Physics*, Vol. 32, p. 483 (1961).

²Babb, Stanley E., Jr., *Rev. Modern Physics*, Vol. 35, p. 400 (1963).

Since the heat conducted away from the DTA cell increases with increasing pressure, a slight misalignment of the sample wells would cause an error in the sample temperature. To check this out a cell was constructed with only two sample wells. The differential temperature was measured in the same manner but the sample temperature was measured directly from the sample as shown in Fig. 3.

Thermograms run on indium after this modification are shown in Figs. 4 - 7. Good agreement was reached on the melting point up to 4000 psi but the 10,000 psi run shows a melting point of 152°C, while according to Babb the melting point should be 159°C at 10,000 psi. The reason for this difference has not been determined but will be investigated.

Thermograms (Figs. 8 - 10) were obtained for nitromethane at ambient, 750, and 1500 psi. The ambient run shows the boiling point at 90°C and no indication of a decomposition exotherm. At 750 psi the boiling point was increased such that the decomposition is shown at 225°C. The thermogram run at 1500 psi shows the decomposition starting about 210°C. A thermogram was run at 4000 psi but there was too much noise to detect any exothermic reactions.

Thermograms (Figs. 11 - 14) of FEF0 were also obtained at ambient, 750, 1500, and 4000 psi. The ambient run shows two exotherms, the first starting at 210°C. The run at 750 psi also shows two exotherms, which are much larger than those obtained at ambient pressure, and at 1500 psi there appeared to be only one large exotherm. At 4000 psi there are two exotherms of approximately equal size with reaction starting at 185°C. This is ~ 25°C lower than that obtained at ambient and 750 psi pressures.

Fig. 3

Schematic Diagram of DTA Cell

Fig. 4
DTA Thermogram
Indium @ 750 psi of N_2
13°C/min.

Fig. 5

DTA Thermogram
Indium @ 1500 psi of N_2
12.5°C/min.

Fig. 6

DTA Thermogram
Indium @ 4000 psi of N_2
11°C/min.

Fig. 7

DTA Thermogram
Indium @ 10,000 psi of N_2
8.5°C/min.

F-17

DSC Thermogram
Nitromethane @ 750 psi of N₂
13°C/min.
Fig. 9

Fig. 10

DTA Thermogram
Nitromethane @ 1500 psi of N_2
12°C/min.

Fig. 11
DTA Thermogram
FEFO @ ambient pressure of N_2
15°C/min.

Fig. 12

DTA Thermogram
FEFO @ 750 psi of N_2
13°C/min.

Fig. 13

DTA Thermogram
FEFO @ 1500 psi of N_2
 $12^\circ\text{C}/\text{min.}$

Fig. 14
DTA Thermogram
FEFO @ 4000 psi of N_2
10°C/min.

LRL personnel requested pressured-DTA runs on $\text{Na}_3\text{PO}_4 \cdot 10 \text{H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$. The ambient pressure thermogram (Fig. 15) of $\text{Na}_3\text{PO}_4 \cdot 10 \text{H}_2\text{O}$ shows two endotherms starting at 68°C and a third endotherm at 100°C which would be the loss of the H_2O . At 250 psi the thermogram (Fig. 16) shows the two endotherms at $\sim 65^\circ\text{C}$ but the third endotherm (H_2O) is at 200°C . The 750 and 1500 psi thermograms (Figs. 17 and 18) show the first two endotherms at approximately the same temperature and the third endotherm is absent. These data indicate that at ambient pressure the endotherms beginning at 68°C are solid-solid transformations and the one at 100°C is the loss of the $10 \text{H}_2\text{O}$.

The $\text{NH}_4\text{H}_2\text{PO}_4$ ambient pressure thermogram (Fig. 19) shows an endotherm at 205°C , and the thermogram (Fig. 20) run at 1500 psi shows an endotherm bottoming occurs at 190°C . Since there is little change in the temperature of this endothermic reaction, as the pressure is varied, a solid-solid transition is indicated.

Fig. 15
DTA Thermogram
 $\text{Na}_3\text{PO}_4 \cdot 10 \text{H}_2\text{O}$ @ ambient pressure of N_2
 $11^\circ\text{C}/\text{min}$.

Fig. 16

DTA Thermogram

$\text{Na}_3\text{PO}_4 \cdot 10 \text{H}_2\text{O}$ @ 250 psi of N_2
13°C/min.

Fig. 17

DTA Thermogram

 $\text{Na}_3\text{PO}_4 \cdot 10 \text{H}_2\text{O}$ @ 750 psi of N_2
14°C/min.

Fig. 18

DTA Thermogram

 $\text{Na}_3\text{PO}_4 \cdot 10 \text{H}_2\text{O}$ @ 1500 psi of N_2
13°C/min.

Fig. 19

DTA Thermogram

$\text{NH}_4\text{H}_2\text{PO}_4$ @ ambient pressure of N_2
11°C/min.

Fig. 20
DTA Thermogram
 $\text{NH}_4\text{H}_2\text{PO}_4$ @ 1500 psi of N_2
12.5°C/min.

Henkin's Time-to-Explosion for LX-09

We were asked to determine the time-to-explosion (TE) for LX-09 Lot Nos. 94-3, 94-4, 94-5, 94-6, 94-7, and 94-8. In addition, Lot Nos. 94-1 and RX-09-CB (Pantex Lot 8023-114G-02) were included in the study for comparison. Lot 94-1 is being used in our coupon test studies and the sample of RX-09-CB was from unit LTU-4A and X-402.

The TE's are given in Table III and a graph of the log of the time versus the reciprocal of the absolute temperature is presented in Fig. 21.

The TE's for Lot Nos. 94-1 and 94-7 are significantly different and they indicate that 94-7 is thermally more sensitive than the other lots, especially 94-1, which is less sensitive than the others.

The chemical analysis of lots 94-1 and 94-7 (Table IV) show some variations in the composition; however, the Henkin's test normally is not sensitive to small changes in sample composition. The TE's will be determined for several lots of RX-09, which vary in composition, to establish if this test is sensitive to change in the HMX, DNPA, and FEFO compositions.

Table III

<u>Lot Number</u>	<u>Time-to-Explosion</u> (seconds)			
	<u>Temperature, °C</u>			
	<u>225</u>	<u>230</u>	<u>237</u>	<u>242</u>
94-1	927	456	344	146
	807	476	313	126
	762	438	314	111
	729	440	343	124
Harmonic mean	(800)	(452)	(327)	(126)
94-3	641	379	235	75
	559	305	236	82
	511	350	272	64
	556	420	220	75
Harmonic mean	(553)	(359)	(239)	(73)
94-4	636	349	127	65
	639	356	219	66
	592	396	202	73
	507	331	244	60
Harmonic mean	(588)	(356)	(186)	(66)
94-5	690	353	233	87
	589	358	245	83
	561	368	216	110
	523	365	156	*
Harmonic mean	(585)	(360)	(206)	(92)
94-6	561	392	234	65
	542	327	248	63
	489	330	233	68
	610	348	238	77
Harmonic mean	(547)	(347)	(238)	(68)
94-7	510	301	217	54
	540	321	211	57
	470	305	208	63
	441	314	168	53
Harmonic mean	(487)	(310)	(199)	(56)
94-8	652	440	222	92
	620	340	217	73
	542	379	235	87
	530	480	219	75
Harmonic mean	(582)	(403)	(223)	(81)
PX Lot 8023 114G-02	559	480	275	135
Part No. 68-1902-019	654	434	246	100
from LTU-4A	712	419	275	114
	775	439	232	108
Harmonic mean	(665)	(442)	(256)	(113)

*No explosion

Table IV

LX-09 Compositions
(Lot Nos. 94-1 and 94-7)

<u>Lot No.</u>	<u>HMX (%)</u>	<u>DNPA (%)</u>	<u>FEFO (%)</u>
94-1	93.18	4.58	2.24
94-7	92.57	5.03	2.40

FUTURE WORK; COMMENTS; CONCLUSIONS

The concentration of the impurities in FEFO is being accomplished by gas chromatography. The runs made using an analytical column (1/8-inch OD x 1 meter with OV-3 on Chromsorb WHP) show a concentration of the low boiling impurities in one fraction and a second fraction containing FEFO with very percentages of impurities.

A sample system is being designed to study the isothermal decomposition of FEFO. Small gas samples (~ 7 cc) can be taken and analyzed by both gas chromatography and mass spectrometry, which will provide a cross-check on the analyses.

Analysis of the atmosphere in several of the coupon test assemblies was made by gas chromatography. Gas chromatography should provide a more accurate analysis on small concentrations than mass spectrometric analysis.

The third compression type sample conditioned at 80°C for 9 months has been disassembled. The LX-09 had lost some of its mechanical strength and had turned a much darker purple. The change in color was unexpected since the HE from the first two assemblies, aged 2 and 5 months at 80°C had faded.

The DTA, pyrolysis, and TGA thermograms of the control and the aged sample show no noticeable differences. The Henkin's time-to-explosion for the 9-month sample showed less deviation from the control than those ages 2 and 5 months.

The high pressure DTA equipment is being checked out to determine the accuracy of the thermocouple used to measure the sample temperature. The melting point of indium was about 7°C low at 10,000 psi. Reasons for this error are being investigated.

Thermograms were run at elevated pressures on FEFO, nitromethane, $\text{NaPO}_4 \cdot 10 \text{ H}_2\text{O}$, and $\text{NH}_4\text{H}_2\text{PO}_4$. FEFO showed two exothermic reactions. Ambient pressure run on nitromethane showed the boiling point but not the decomposition exotherm; however, at 750 psi the boiling point is increased allowing decomposition at 225°C to be observed.

By running DTA thermograms on $\text{NaPO}_4 \cdot 10 \text{ H}_2\text{O}$ and $\text{NH}_4\text{H}_2\text{PO}_4$ at ambient and elevated pressures, the endotherms resulting from the loss of H_2O can be determined from those involving solid-solid transformations.

The Henkin's time-to-explosions (TE) were obtained on several production lots of LX-09; two lots (94-1 and 94-7) show significant differences in their TE. The chemical composition differs some but the TE's are not normally sensitive to small changes in sample composition. Additional tests are planned to determine if there is a correlation between the chemical composition and the TE.