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THERMAL PROPERTIES OF EXPLOSIVES

The purpose of this project is to determine the thermal properties of explosives, and to continue the development and evaluation of thermal tests.

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ABSTRACT

Two preliminary experiments were conducted to determine (1) how the time-to-explosion (TE) using Lee Plugs (short stainless steel and aluminum) would compare with the TE obtained using the lead plugs; and (2) how the Lee Plugs would perform with du Pont's EL-511 and Tacot at 314°C. and 362°C., respectively.

The Pantex-built gas chromatograph is operating as a two-column instrument, and the findings of an extensive check out of the instrument are reported. The chemical reactivity test sample holders were shown to evolve approximately 30 μ l of $N_2 + O_2$ and 3 μ l of CO_2 when heated at 120°C. for 22 hours.

A number of thermal tests were made on two lots of LX-04-1 (39A and 38B) to determine if any differences could be detected that would explain why Lot 38B tensile strength is much better than 39A when both were made from the same lot of Viton A. Some differences were detected, but they have not been related to the tensile strength of the material.

The time-to-explosion for various Adiprenes with HMX are reported, and they indicate that there could be some reactivity between the Adiprene and HMX.

Pantex and LASL DTA thermograms and pyrolograms for PETN and Extex are reported for comparison to determine how the sensitivity of Pantex instruments compare with LASL, and if these instruments could be used to qualify PETN and Extex in accordance with LASL Specification 13Y-104481.

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A series of thermal tests were conducted on a LRL formulation (RX-04-BV) to determine if it was more sensitive than LX-04-1, and the results of the tests indicate that it is no more, and possibly less, sensitive than LX-04-1. The progress of the study of PBX binders and desensitizers is reported along with a list of those samples now being investigated.

PREVIOUS APPLICABLE WORK

The search for a loading technique for the Henkin test that would allow times-to-explosion to be obtained at temperatures above 327°C. (the melting point of the lead plugs) was continued this quarter. Last quarter some tests were conducted with Lee Plugs, and this testing has continued this quarter.

The fabrication of a gas chromatograph at Pantex was started several quarters ago, and it is now in operation as a two-column instrument.

The study and evaluation of explosives with the thermal test at Pantex has continued, and the data obtained for several different explosives are reported this quarter.

DISCUSSION

HENKIN TEST

Last quarter a preliminary test was conducted to determine if the Lee Plugs would provide a satisfactory seal in the blasting caps, thus allowing the upper temperature limit for the Henkin test to exceed that imposed by the lead plug system. This test indicated that the long Lee Plugs, both stainless steel and

aluminum, would not seal as well as the short Lee Plugs. The time-to-explosion (TE) obtained with the short stainless steel and aluminum plugs were different; therefore, an additional test was run this quarter to determine which short Lee Plug would give a better seal and approximately the same TE as the lead plug system. Analysis of these test data (Table I) indicates that the stainless steel plugs give better results because: (1) the TE at 250°C. and 261°C. are approximately the same as the TE for the lead plugs; (2) the ratio of the maximum spread to the harmonic mean for the stainless steel plug is a minimum at all temperatures except 250°C., and at this temperature it is only slightly larger than the ratio for the lead or aluminum plugs.

At temperatures above 290°C., the Wood's metal oxidizes too quickly; therefore, the bath material was changed to tin which reacted with the brass blasting cap. This problem was solved by chrome plating the outside of the caps.

To determine if the stainless steel and aluminum Lee Plugs would work at higher temperatures, du Pont EL-511 and Tacot were tested. The data from these tests are given in Table II. The Tare Tacot sealed with the stainless steel plugs failed to expode, and the cause of this failure is not yet known, but will be investigated next quarter.

Table I

Time-to-Explosion for HMX with Various Plugs

	<u>229°C. (sec)</u>	<u>235°C. (sec)</u>	<u>242°C. (sec)</u>	<u>250°C. (sec)</u>	<u>261°C. (sec)</u>
Lead Plug	375	252	196	113	49
Pressed at 350 lbs.	435	291	172	102	43
	370 T	306	215	99	49
	300	280	167	113	57
Harmonic Mean	364	281	186	106	49
Maximum Spread	135	54	48	14	14
Ratio of max. spread to harmonic mean	.37	.19	.26	.13	.29
Lead Plug	295	186	129	72 T	38
Pressed at 800 lbs.	397	182	151	68 T	43
	275	244	125	70	41
	460 T	211	118	67	39
Harmonic Mean	341	203	130	69	40
Maximum Spread	185	62	33	5	5
Lee Plug - Short Al	378 T	145	122	86	30
Pressed at 800 lbs.	750 NE	210	138	82	30
	340 T	195	122	76	32
	248	167	164	76	35
	307				
Harmonic Mean	311	176	135	80	32
Maximum Spread	130	65	42	10	5
Ratio of max. spread to harmonic mean	.42	.37	.31	.13	.16
Lee Plug - Short Stain- less Steel - Pressed at	541	319	199	114	53
800 lbs.	744	320	200	97	52
	551	354	206	99	52
	647	323	192	113	59
Harmonic Mean	610	328	199	105	54
Maximum Spread	203	35	14	17	7
Ratio of max. spread to harmonic mean	.33	.11	.07	.16	.13

T blew plug out the top
NE No explosion

Table II

Time-to-Explosion for EL-511 & Tacot

	<u>314°C. (sec)</u>		<u>362°C. (sec)</u>
EL-511 α	49	Tacot, Tare	300 NE
Stainless Steel	38	Stainless Steel	300 NE
Lee Plugs pressed	39	Lee Plugs pressed	300 NE
at 800 lbs.	42	at 800 lbs.	
EL-511 β	59	Tacot, Zebra	300 NE
Stainless Steel	82	Stainless Steel	59
Lee Plugs pressed	106	Lee Plugs pressed	59
at 800 lbs.	120	at 800 lbs.	
EL-511 α	27	Tacot, Tare	38 T
Aluminum Lee Plugs	31	Aluminum Lee Plugs	28 T
pressed at 800 lbs.	39	pressed at 800 lbs.	35 T
	37		
EL-511 β	73	Tacot, Zebra	38 T
Aluminum Lee Plugs	70	Aluminum Lee Plugs	32
pressed at 800 lbs.	66	pressed at 800 lbs.	34
	83		

T -blew plug out the top.
NE-no explosion

GAS CHROMATOGRAPH

The Pantex-built gas chromatograph is now operating as a two-column instrument. The instrument was given an extensive check out, and it was determined that the Perkin-Elmer gas sampling valve, which is to be used to calibrate the GC, has a significant internal volume ($\approx 150 \mu\text{l}$). Therefore, a syringe injection system was built to allow the gas sampling valve and its sample loop to be calibrated as a unit. In addition to calibrating the sampling valve and loop, several attenuation ranges were calibrated, and the calibration value for these attenuation ranges were in agreement with each other (i.e. the attenuation ranges are linear).

An analysis of the gas contained in the empty sample container for the chemical reactivity test after it has been washed, dried, evacuated, filled with helium, and heated at 120°C . for 22 hours shows approximately $30 \mu\text{l}$ of $\text{N}_2 + \text{O}_2$ and $3 \mu\text{l}$ of CO_2 . This is probably due to gas on the inner walls of the sample container being released when the container is heated. When sample containers are treated in a like manner but not heated, an analysis of the gas shows very little of these gases ($< 4 \mu\text{l}$ of $\text{N}_2 + \text{O}_2$ and no CO_2).

A series of runs are being made to determine if the amount of gas evolved from the empty container after it has been cycled was constant, and if it is, then corrections can be made when samples are run.

THERMAL DATA

LX-04-1, Lots 39A and 38B - Pantex was requested by LRL personnel to run a series of thermal tests on two lots of LX-04-1 (39A and 38B) to determine if any differences could be detected that might explain why 38B tensile strength is much better than 39A. Both lots have good densities and were made from the same lot of Viton A (Lot 16), but different batches of HMX.

The DTA thermograms (Figures 1 and 2) of 39A and 38B show that the β to δ transition and the HMX decomposition for 38B occurs at a lower temperature. Additional verification of this was obtained when a DTA thermogram (Figure 3) was made using 38B as the reference and 39A as the sample. Another run was made using 39A as the reference and 38B as the sample, and this also shows the changes to occur in 38B first, which indicates that the differences are not due to instrumentation but are actual differences between the samples.

The pyrolograms of 38B and 39A (Figures 4 and 5) show a small peak at $\approx 190^{\circ}\text{C}$. and 200°C ., respectively. Several duplicate runs were made and each showed this 10°C . difference. The peaks are in the temperature range which one would expect Compound "C" to decompose, and it appears that they might be dependent on the HMX β to δ polymorphic transition (i.e. the DTA thermograms and pyrolograms indicate that the transition and peak occur in 38B first). Also, when a sample of β HMX is converted to δ by heating at these rates, the crystal cracks (the δ polymorph is less dense), and this would permit the gas to escape.

Samples of Lot 16 Viton A were put through the DSC-1, and the thermogram (Figure 6) shows a small endotherm near 100°C . When the sample was recycled, the endotherm did not appear, but after the sample has been exposed to room conditions for about

twelve hours, the endotherm reappeared. The pyrologram (Figure 7) of the Viton shows a broad peak near 100°C., which indicates that a gas is given off. The results of these two tests indicate that the Viton picks up moisture from the air. A sample of Viton will be put through TGA to determine the amount of water given off.

The DTA thermograms and pyrolograms of the various batches of HMX used in making the two lots of LX-04-1 do not show any unusual differences. Other tests (DSC-1, TGA, and chemical reactivity) will also be made on these two lots of LX-04-1 and their components.

Adiprene - HMX - It was reported last quarter that the DTA thermogram of mixtures of Adiprenes and HMX's showed the exothermic reaction to be about 25°C. lower than HMX. This quarter the time-to-explosion for HMX and Adiprene-HMX mixtures were determined, and these data (Table III) also indicate that the mixtures are reactive to some extent.

By the criteria given in a previous report¹ for a reactivity coefficient, the Adiprene-HMX mixture would be classified as borderline reactivity.

The necessary equipment is being obtained for an experiment this next quarter to determine what happens to the nitric oxide when it is exposed to a sample of Adiprene at 120°C. for 22 hours.

¹3rd Quarterly Report for 1963

Table III

Time-to-Explosion for Various Adiprenes with HMX

	<u>240°C. (sec)</u>	<u>261°C. (sec)</u>
Adiprene L-100 + HMX	90 T 82 84 T 84 T	28 30 32 T 31 T
Adiprene L-167 + HMX	88 T 106 94 115 T	30 T 29 34 31 T
Adiprene L-100 cured with acetic acid + HMX	116 84 T 83 T 90 T	32 T 29 T 31 T 32
Adiprene L-167 cured with acetic acid + HMX	93 106 122 103	35 T 32 T 36 34 T
HMX	154 151 152 128	49 41 36 33

T - blew plug out top

Figure 1
LX-34-1
(SR-318-11)
11°C./Minute

Figure 2
LX-34-1
(SR-318-11)
11°C./Minute

PETN-Extex Qualification Test - One part of LASL specifications (13Y-104481) for the qualification of recrystallized PETN and Extex required each to be run in the DTA and pyrolysis apparatus. For comparison, the DTA thermograms of PETN produced at Pantex and LASL (both use ≈ 10 mg samples) are given in Figures 8 and 9, respectively. By comparing the size of the PETN endotherm at 135°C. , the sensitivity of the two instruments can be compared, and since the endotherm are approximately equal in size, it is concluded that the two instruments are operating near the same sensitivity. Therefore, our DTA should be adequate to qualify PETN and Extex.

The Pantex pyrolysis apparatus is much more sensitive than LASL, and to produce similar curves, it was necessary to reduce the recorder sensitivity by a factor of 40.

Figures 10 and 11 are pyrolograms of PETN (20 mg samples) recrystallized here at recorder deflection sensitivity of 0.5 mv/inch and 20 mv/inch, respectively. If the latter pyrologram (Figure 11) is compared to Figure 12, a LASL pyrologram of PETN (10 mg samples), one sees that the PETN decomposition peaks are near the

Figure 12
PETN 10 mg
10°C./Minute
(Reproduction
of LASL Data)

Figure 13
Extex 5118-37
(PETN 5043)
11°C./Minute

PETN Impurities - The pyrologram of Army Grade PETN before recrystallizing is shown in Figure 15. This pyrologram has two impurity peaks around 130°C., but after it has been recrystallized, the pyrologram (Figure 10) shows only one large peak at 130°C. Therefore, it appears that an impurity has been concentrated and experiments will be conducted next quarter to analyze this impurity.

RX-04-BV - LRL personnel requested Pantex to run a series of thermal tests on RX-04-BV; a formulation of HMX, aluminum, and Viton with 66.9%, 13.7%, and 19.4%, respectively.

After comparing the DTA thermograms (Figures 16 and 2) of RX-04-BV and LX-04-1, there is no indication that the RX-04-BV is any more sensitive than LX-04-1. The pyrologram (Figure 17) of RX-04-BV has a small peak near 200°C., which is probably Compound "C", but when compared with the pyrologram (Figure 4) of LX-04-1, one sees that the two evolve gas at about the same rate which is also another indication that the sensitivity of RX-04-BV is about the same as LX-04-1. The time-to-explosion (TE) for RX-04-BV and HMX are given in Table IV, and the TE for RX-04-BV are longer than HMX, which indicates that this formulation is slightly less sensitive than HMX.

Table IV

Time-to-Explosion for RX-04-BV & HMX

	<u>243°C.</u> <u>(sec)</u>	<u>250°C.</u> <u>(sec)</u>	<u>255°C.</u> <u>(sec)</u>	<u>261°C.</u> <u>(sec)</u>	<u>267°C.</u> <u>(sec)</u>
HMX Class A	195 T	113	82	49	27
(lead plug	158	102	88 T	43	29
pressed at	184	99	71	49 T	28
350 lbs.)	134	113	72	57	26
 RX-04-BV	 402	 215	 162	 70	 31
(lead plug	467	268	136	70	31
pressed at	425	220	165	68	30
350 lbs.)	374	214	154	70	36

T - blew plug out top.

PBX Binders & Additives - A number of materials which could possibly be used with explosives and binders or desensitizers are being run in the DSC-1 and the pyrolysis apparatus. The purpose of running these in the pyrolysis is to determine the temperature at which they start to decompose so that the sample may be thermally cycled in the DSC-1 to determine if certain transitions are dependent on the thermal history of the sample. These data obtained with the DSC-1 should help to obtain a better understanding as to why some materials desensitize an explosive, and what changes might be expected in the percentage crystallinity as the sample is thermally cycled.

The following is a list of the samples that are currently available for testing:

Fluorel KF-2141	Kel-F 800
Viton B	Kel-F 827
Viton A	Estane
Beeswax	Firestone Diene
Kynar 16	Kel-F 3700
Aclar 22	Polyethylene, AC #400
Aclar 33	Polyethylene, AC #0
Firestone Exon 461	Epolene N-11
Kel-F 81	Epolene E-14

The pyrolograms of all the samples have been completed, and about half of the samples have been run in the DSC-1. These data should be more convenient for the reader if it is all reported at one time; therefore, the DSC-1 thermograms will be completed next quarter and all the data will be reported at that time.

FUTURE WORK; COMMENTS; CONCLUSIONS

The time-to-explosion (TE) data obtained with the stainless steel Lee Plugs appear to be better than that obtained with the aluminum Lee Plug. The stainless steel and lead plug gave TE that were approximately the same at 250°C. and 261°C. The ratio of the spread to the harmonic mean of the TE for the stainless steel Lee Plugs was less (in all but one case, i.e. 250°C.) than the ratio for lead or aluminum plugs. Both types of plugs will continue to be used for a while longer to be certain that the stainless steel are better.

The Pantex-built gas chromatograph is operating as a two-column instrument, and it has been calibrated. The chemical reactivity sample holders are being run to determine if the gas evolved by an empty sample holder is constant, and would permit corrections to be made for this gas when samples are run.

The thermal tests that were run on Lots 39A and 38B of LX-04-1 have detected some difference between the two samples such as (1) 38B β to δ transition occurs at a lower temperature than 39A; (2) the 38B exotherm occurs a few degrees earlier than 39A; (3) the Compound "C" peak observed on the Lot 38B pyrologram is about 10°C. earlier than 39A. None of these differences would appear to be related to the mechanical strength of the sample. Next quarter the times-to-explosion will be determined and other tests (DSC-1, TGA, and chemical reactivity) will also be run on these two lots of LX-04-1 and their individual components.

The time-to-explosion (TE) for mixtures of various Adiprene (L-100, L-167, L-100 + acetic acid, and L-167 + acetic acid) with HMX are shorter than TE for HMX,

which indicates that the mixture might be reactive, and the reactivity coefficient would classify the mixture as borderline reactivity. The necessary equipment is being obtained for an experiment next quarter to determine what happens to the nitric oxide when it is exposed to a sample of Adiprene at 120°C. for 22 hours.

Pantex DTA and pyrolysis can produce curves for PETN and Extex that compare very closely to those produced by LASL. Therefore, these two instruments can be used to qualify PETN and Extex in accordance with a LASL specification (13Y-104481).

When a sample of recrystallized PETN is run in the pyrolysis, an impurity peak is observed near 130°C. The pyrologram of Army Grade PETN, which was used to make the recrystallized sample, does not have a peak as large as the recrystallized sample which would appear to indicate that the impurity is being concentrated. Studies will be made in the future to determine what impurity is causing this peak.

The sample of RX-04-BV that LRL requested Pantex to test was run in the DTA, pyrolysis, and Henkin and each indicated that the thermal sensitivity of the sample was about the same as LX-04-1.

The study of PBX binders and desensitizers will be completed next quarter, and all the data (pyrolograms and DSC-1 thermograms) will be reported.