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THERMAL PROPERTIES

MASTER

L. C. Myers

DEVELOPMENT DIVISION

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Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 647
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806-335-1581

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ABSTRACT

The thermal decomposition investigation of PETN using an LX-13 type PETN was begun this quarter. Samples are being conditioned at 373, 353 and 333 K and others will be conditioned at 393 and 383 K. Data from five samples are reported.

A series of chemical reactivity tests was made using PETN to determine if decomposition rates could be calculated from the results. The data fit a semilogarithmic plot of the gas evolved as a function of time reasonably well.

The last of a series of HNAB and PETN samples was evaluated to determine if the two are compatible. These samples were conditioned at 80 C for 26 and 25 months and showed no indication of reactivity.

The investigation into methods of improving the chemical reactivity test data has continued and a source of a small variation in the instrument sensitivity was determined.

DISCUSSION

THERMAL DECOMPOSITION OF PETN

Last quarter it was reported that a sample of LX-13 type PETN had been specially prepared for this thermal decomposition study. This sample was prepared by two recrystallizations of a DuPont mil spec PETN before it was made into the LX-13 type.

To minimize the number of leaky sample containers, glass sample vials with ball joints and break seals were purchased for this investigation. A drawing of the sample vial is shown in Fig. 1. One-half (0.50) gram of PETN was placed into the vials, they were evacuated, then backfilled with helium to 53 kPa (400 torr). The vials were then sealed with a torch. If the initial pressure in the vials was greater than 53 kPa the heat from the torch would increase the pressure above atmospheric and the glass would be blown outward rather than collapsing to form the desired seal.

The test temperatures selected for this investigation are 393, 383, 373, 353 and 333 K. Twelve samples will be conditioned at each temperature and there will be five ambient control samples. Samples were placed in ovens at 373, 353, 333 K on December 8, 1975.

After a PETN sample has been conditioned for the desired time it is removed from the oven, the gas is removed and its volume is determined by using a vacuum/gas manifold equipped with a toepler pump, gas burette and manometer. Having determined the total volume of gas it is transferred to a sample loop for analysis by gas chromatography thus determining the composition and total volume of gas evolved.

Some data have been obtained from the 373 and 353 K samples and these are given in Table I. A plot of the logarithm of the total volume of gas evolved as a function of time is given in Fig. 2.

Before conditioning the samples at 393 and 383 K, chemical reactivity tests were made at 393, 383 and 373 K for varying times to obtain preliminary data on the rate of decomposition of this sample of PETN. These results are given in Table II. A plot of the logarithm of the volume of the evolved gas as a function of time is linear. This plot is shown in Fig. 3 and the 393 and 373 K data fit a straight line but the 383 K data do not fit as well. The lines of best fit were determined and are given in Table III.

From the results given in Table II 0.50 g of PETN at 393 K would be expected to evolve about 0.334 ml of gas in 48 hours. However, ten samples (in glass vials) were placed in an oven at 393 K and as an extra safety precaution each sample vial was placed in a 2.54 x 15.25 cm steel pipe with a cap on one end. The temperature of the oven was continuously monitored with two thermocouples, one touching a steel pipe which contained the sample vial and the other thermocouple was about 30 cm above the sample monitoring the oven air and located next to a mercury thermometer used to check the accuracy of the thermocouples. The recording of the thermocouple output showed a 5° overshoot for about 40 minutes (average 2.5 K above 393 K for 40 minutes). After 48 hours the oven was opened to remove a sample vial for analysis and eight of the ten vials had burst from excessive pressure. The other two had only a small part of the PETN left. The two intact vials had small pin holes in the seal area which prevented them from bursting. The recorder trace of the thermocouple output gave no indication of any change in the oven temperature during the 48-hour period. After reviewing all of the available data only two possible causes appeared feasible. These are (1) the 5° - 40 minute overshoot accelerated the decomposition and/or (2) the sample was large enough to produce self-heating which accelerated the decomposition.

Both of these theories will be evaluated in the near future with chemical reactivity tests at 398 K and the temperature profile within the PETN sample will be calculated using a computer program.

HNAB-PETN REACTIVITY INVESTIGATION

About two and one-half years ago LLL personnel requested Pantex to conduct a series of coupon tests to determine if HNAB and PETN were compatible. The coupon samples were 2.54 cm in diameter and approximately 3.2 mm thick. The HNAB pellet was sandwiched between two PETN pellets. The last of this series (conditioned for 26 months at 353 K) was disassembled this quarter. The HNAB and PETN pellets show no indication of being reactive. A photograph of the PETN and HNAB pellets is shown in Fig. 4.

Shortly after the above series of tests was started it was determined that HNAB dissociates in an acetone-water solution to form trinitrobenzene and picric acid. Chemical reactivity tests using picric acid

and PETN show the two to be very reactive. Therefore, HNAB and PETN sandwiches were sealed in an atmosphere containing acetone and water vapors to determine if the HNAB would dissociate to produce picric acid which would react with PETN. The last of these containers (conditioned for 25 months at 355 K) were disassembled and the appearance of the pellets was identical to those shown in Fig. 4, which were stored in a dry atmosphere.

The condition of these pellets indicates that PETN and HNAB are compatible and can be stored together for extended periods of time without reacting.

ADHESIVES EVALUATION

Last quarter a series of tests was conducted with three LLL formulated adhesives to determine if they are reactive with LX-10 and RX-03-BB. This quarter samples of the three adhesives were run in the thermal mechanical analyzer. These data are shown in Fig. 5. Samples HGH-14 and HGH-18 have a glass transition at 195 K and 223 K, respectively. The TONOX cured sample gave little or no indication of a glass transition and its coefficient of thermal expansion is less than the other two adhesives.

IMPROVEMENTS FOR THE CHEMICAL REACTIVITY TEST APPARATUS

There is a continuing effort to improve the repeatability of the results from the chemical reactivity test. This quarter several runs were made using a thermal conductivity detector control unit from another Varian chromatograph. The control unit contains the power supply, a portion of the bridge circuit and controls for the detector. The variations from these two units were essentially the same. The majority of the day to day variations in sensitivity were from 1 to 2% but on occasion there were variations as large as 8%.

The power supply voltage for the thermal conductivity detector was monitored and there was no apparent correlation between the voltage and an 8% variation in sensitivity. However, small variations in the power supply voltage did correlate with the variations in the sensitivity for any given day. Both voltage and sensitivity would increase about the same order of magnitude ($\sim 1\%$) during the day. This probably results from variations in the temperature of the electronics (power supply).

FUTURE WORK, COMMENTS, CONCLUSIONS

A batch of specially prepared PETN was made to investigate the thermal decomposition of PETN. One-half gram samples of PETN were sealed in glass vials with a helium atmosphere. These samples are being conditioned at 373, 353 and 333 K and the data for four samples conditioned at 373 and one sample conditioned at 353 K are reported.

The PETN samples (in glass vials) which were conditioned at 393 K for 48 hours evolved enough gas to burst the containers. Chemical reactivity test data on this batch of PETN indicate that it would take several days for the sample to evolve sufficient gas to burst the containers.

An investigation was started to determine the cause of the high decomposition rate at 393 K.

Chemical reactivity test data were obtained from PETN at 393, 383 and 373 K for varying times and a semilogarithmic plot of the gas evolved as a function of time is linear.

The last of the samples from the HNAB-PETN sample study has been evaluated. These samples were conditioned at 355 C for 26 months and there were no indications of any reaction between these two explosives.

The thermal mechanical analysis test was run on three LLL-formulated adhesives. Two of the adhesives, HGH-14 and HGH-18 have glass transitions at 195 K and 223 K, respectively, and the formulation cured with TONOX showed no indication of a glass transition in the 193 to 363 K temperature range. Therefore, from the TMA data TONOX would be the best of the three.

Some of the variations in the sensitivity of the chemical reactivity test apparatus correlates with variations in the thermal conductivity detector voltage. This is probably due to changes in the temperature of the electronics.

An internal standard run with each sample may be required to further reduce variations in the chemical reactivity test results. This could be accomplished by adding a gas sampling valve and introducing a known volume of some gas with each sample. The best gas to use would probably be neon because its retention time is less than the gaseous products which are normally analyzed.

Fig. 1. Glass Sample Vial for Thermal Decomposition Studies

Table I. Gas Evolved from 0.50 g of PETN

(Volumes in mL corrected to STP)

<u>Time</u> <u>(Days)</u>	<u>Temp.</u> <u>(K)</u>	<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>
9	373	0.060	0.067	0.008	0.105	0.043	0.283
15	373	0.118	0.135	0.033	0.265	0.095	0.645
22	373	0.212	0.189	0.031	0.524	0.150	1.108
22	373	0.227	0.210	0.043	0.497	0.146	1.123
22	353	0.004	0.019	0.016	0.005	0.002	0.046

Fig. 2. Logarithm of Total Volume of Gas Evolved from PETN as a Function of Time

Table II. Chemical Reactivity Test Data for PETN
(ml of gas evolved from 0.250 g corrected to STP)

<u>Time</u> <u>(Hrs)</u>	<u>Temp.</u> <u>(K)</u>	<u>N₂</u>	<u>CO</u>	<u>NO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>Total</u>	<u>Total</u> <u>Less</u> <u>N₂</u>
22	393	0.032	0.018	0.012	0.026	0.009	0.097	0.065
22	393	0.025	0.017	0.012	0.023	0.008	0.085	0.060
46	393	0.052	0.047	0.017	0.069	0.030	0.215	0.163
46	393	0.063	0.053	0.008	0.074	0.032	0.230	0.167
70	393	0.121	0.131	0.026	0.176	0.054	0.508	0.387
70	393	0.120	0.129	0.020	0.178	0.056	0.503	0.383
46	383	0.015	0.005	-0-	0.007	0.002	0.029	0.014
46	383	0.019	0.006	-0-	0.007	0.002	0.034	0.015
94	383	0.037	0.023	0.002	0.027	0.012	0.101	0.064
94	383	0.035	0.023	-0-	0.026	0.012	0.096	0.061
163	383	0.048	0.046	0.009	0.066	0.030	0.199	0.151
163	383	0.046	0.048	0.011	0.068	0.032	0.205	0.159
94	373	0.017	0.002	-0-	0.004	0.001	0.024	0.007
94	373	0.011	0.002	-0-	0.004	0.001	0.018	0.007
190	373	0.012	0.008	-0-	0.012	0.003	0.035	0.023
190	373	0.017	0.008	-0-	0.012	0.003	0.040	0.023
286	373	0.027	0.017	0.020	0.029	0.011	0.104	0.077

Fig. 3. Logarithm of Gas Evolved from 0.250 g of PETN as a Function of Time

Table III. Gas Evolution from PETN as a Function of Time

(Volume (v) in ml Corrected to STP and Time (t) in Hours)

<u>Temperature (K)</u>	<u>Equation</u>
393	$v = 0.0377 t + 3.3079$
383	$v = 0.02003 t + 1.9192$
373	$v = 0.01249 t + 0.76882$

Fig. 4. Coupon Test Samples of PETN and HNAB
Conditioned at 353 K for 26 Months

Fig. 5. Thermal Mechanical Analysis of Three LLL-Formulated Adhesives
Heating Rate 5 K/min