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THERMAL STABILITY OF A HAN-BASED LIQUID GUN PROPELLANT

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Abstract

Experiments to determine the effect of surface area, head space, and containment on liquid gun propellant degradation at temperatures of 100 and 148°C were conducted. The conclusions from these tests are that an increased surface area in LP containment can significantly increase the rate of LP decomposition. The head space is not a significant factor in altering the rate of degradation, but if the gaseous products are allowed to escape, the degradation rate is significantly lowered.

Keywords: hydroxyl ammonium nitrate based liquid gun propellant, thermal stability

Introduction

Understanding the thermal stability characteristics of an experimental hydroxyl ammonium nitrate (HAN) based liquid gun propellant (LP) is necessary for avoiding the conditions under which an unscheduled cookoff could occur. One method for defining these conditions is to determine the kinetic decomposition parameters through experimental techniques and applying these parameters to a model for predicting cookoff at larger and full scale configurations. The Frank-Kamenetskii model is used when there is only conductive heat transfer. The Semenov model is used where there is conductive and convective heat transfer.

A prior study [1] determined the kinetic parameters of LP at high temperature [205 and 68°C]. The LP samples were carefully syringed into capillary tubes and centrifuged. The capillary (5 μL) was placed in a wider glass tube which was flame sealed. This container arrangement was immersed in an oil bath which was maintained at the selected temperature to ±1°C. The LP was carefully monitored and timed until a brown gas was observed, which is an indicator of complete decomposition.

A pseudo-Arrhenius plot was constructed by plotting the natural logarithm of the time-to-brown (in seconds) *vs.* the inverse of the temperature of decomposition (Fig. 1). In this plot there is a shift in the slope at about 125°C. Since the lower temperature kinetics are more useful for predicting safe storage temperature, only the data collected below 125°C were used for calculating the activation energy and pre-exponential factor: $E_a = 162.2$ kJ mol^{-1}; $A = 3.61\times10^{17}$ s^{-1}.

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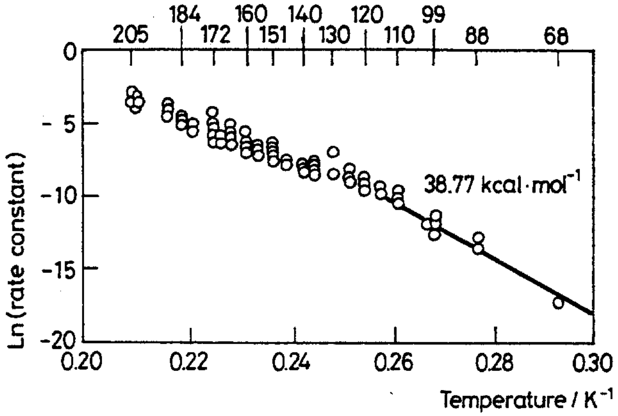

Fig. 1 LP Arrhenius plot

A series of slow cookoff tests were conducted on the LP at varying quantities and container dimensions to correlate the predicted cookoff temperature with the actual cookoff temperature. The results of these tests are given in Table 1.

Table 1

Container	Runaway temperature					
	ml LP	psi	predicted/°C	observed/°C	min	diameter
Al pipe & glass liner	19	100	114	110	3651	0.8
SS pressure bomb	300	sealed	93	96	339	3.18
1 L glass flask	1000	ambient	116	112	7450	6.2
5 gal PE drum	17400	ambient	117	127	5700	13.75

*Frank Kamenetskii, conductance only

**Semenov, conductance and convection

In general the predicted cookoff temperatures were higher than the observed cookoff temperature for the smaller containers and lower than the observed cookoff temperatures in the larger containers. It was postulated that this discrepancy may be due to increased reaction as a result of an increased surface/volume ratio in the smaller containers or that the head space in the LP container may also affect its reactivity. This prompted the following study to be conducted.

Experimental

The first series of tests contained LP in capillaries at varying surface to volume ratios and head spaces. They were placed in an oven at 100°C for 80 h. The LP was then analyzed by liquid chromatography for % HAN and % Triethanol ammonium nitrate (TEAN) remaining, based on 100% HAN and 100% TEAN in the LP at the

1) Sample Size/Container Volume: 7 μL/0.35 mL
Ratio of LP to Container Volume: 1/50
Number of samples: 7
%HAN/%TEAN remaining after 80 h at 100°C based on
100% HAN and 100% TEAN at start of test: **0/0, 0/0, 0/0, 50/79, 41/83, 40/68, 51/81**

2) Sample/Container: 7 μL/2.1 mL
Ratio: 1/300
Number of samples: 2
%HAN/%TEAN: **93/92, 81/82**

3) Sample/Container: 6(7 μL)=42μL/2.1mL
Ratio: 1/50
Number of samples: 3
%HAN/%TEAN: **0/0, 0/0, 0/0**

4) Sample/Container: 42μL/2.1mL
Ratio: 1/50
Number of samples: 1
%HAN/%TEAN: **83/81**

5) Sample/Container: 42μL/2.1mL
Ratio: 1/150
Number of samples: 3
%HAN/%TEAN: **90/91, 86/87, 98/95**

6) Sample/Container: 7 μL/5 mL
Ratio: 1/714
Number of samples: 3
%HAN/%TEAN: **71/80, 77/80, 58/80**

7) Sample/Container: 144 μL/5 mL
Ratio: 1/35
Number of samples: 2
%HAN/%TEAN: **73/83, 85/82**

8) Sample/Container: 7 μL/10 mL
Ratio: 1/1430

9) Sample/Container: 144 μL/5 mL
Ratio: 1/35

Fig. 2 %HAN/%TEAN remaining after 80 h at 100°C

beginning of the test. Figure 2 shows a summary of the container setup, sample volume, container volume, ratio of LP to container volume, the number of samples per configuration, and the % HAN and % TEAN remaining after the experiment for each of the samples.

Configuration 1 in Fig. 2 had quite a bit of variability in the results. Three of the samples completely decomposed while in the remaining four, approximately 50% of the HAN decomposed. In configuration 3, the LP samples divided among 6 capillaries all decomposed. One sample in configuration 8 also completely decomposed, but the second sample in the same configuration decomposed only ~15%. The other configurations showed only minor differences in the rate of decomposition.

A second series of tests evaluated the effect of three containers on the degradation of LP. Samples of 7 μL of LP were placed in flame sealed capillary tubes, flame sealed ampoules and screw cap vials. They were placed in a 100°C oven for 5.6 days and analyzed for % HAN remaining. The results shown in Fig. 3 reveal that the flame sealed glass containers all completely decomposed under these conditions, whereas the screw-cap vials exhibited little decomposition. Since one of the LP degradation products, NO_2, greatly catalyzes LP decomposition, this result was not surprising. The flame sealed containers provided no opportunity for the NO_2 gas to escape, whereas the screw cap vials did.

In the final series of experiments the effect of increased surface area with the LP is measured. In this case, the control samples have the same configuration as the first example Fig. 2. The coated and uncoated samples had an extra length of glass tubing on top of the capillary and inside the tube. For the coated sample, the tubing was wetted with the LP. For the uncoated sample, care was taken to keep the glass tubing clean. The capillaries were placed in a 148°C oven and timed for complete decomposition (presence of brown fumes). The results of this test are shown in Fig. 4. The time-to-brown for the control and the uncoated samples were virtually the same, where the coated samples decomposed four times faster.

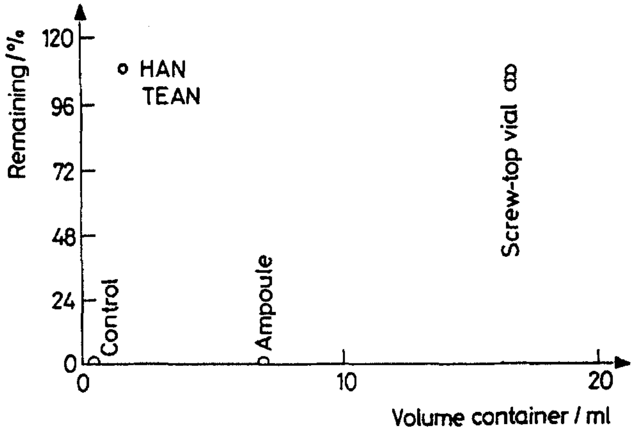

Fig. 3 % HAN and TEAN remaining after 7 µL LP heated @ 100°C for 5.6 days in capillary tubes, ampoules, and screw cap vials

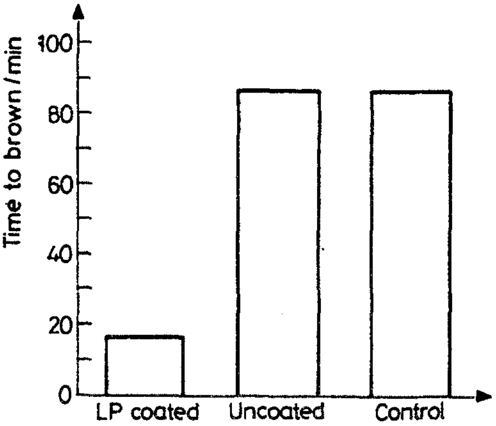

Fig. 4 Effect of surface area on LP decomposition glass tube @ 148°C

Conclusions

The experiments showed that LP degradation may be significantly increased if the surface to volume ratio is very high, which is an indication of reactivity with glass. The degradation rate, however, may be lowered if the gaseous products, such as NO_2, are able to escape the container. The experiments conducted did not show that head space in a sealed system significantly alters the degradation rate.

Since the experimental conditions for deriving the kinetic parameters used a sealed system and a relatively high surface area, the actual degradation rate in a full scale vented container may be lower. In fact, for the 5 gallon cookoff test, the actual cookoff temperature was 10°C higher than that predicted. However, the remaining tests produced observed cookoff temperatures within 4°C of the predicted cookoff temperature. This would indicate the experimentally derived kinetic parameters are reasonably accurate in this temperature range.

References

1 'Thermal Stability Analysis of HAN-Based Liquid Gun Propellants' by J. C. Oxley, J. L. Smith, J. A. Askins, N. S. Gilson, H. Feng, M. Banks, (NMIMT), & J. S. Gardner. 1993 JANNAF Hazard Subcommittee Meeting, 11–13 May 1993, Fort Lewis, Washington.