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Summary
Small-scale safety testing has been completed on 3,3'-diamino 4,4'-azoxyfurazan (DAAF). The relative sensitivity of DAAF against various stimuli was evaluated. DAAF shows no observable sensitivity to friction or static spark. It has impact sensitivity approaching that of TATB. Using the One Dimensional Time to Explosion (ODTX) apparatus to measure thermal response, DAAF shows similar sensitivity to TNT and HMX. DSC and the CRT were also used to evaluate the thermal stability of DAAF under various conditions.

Introduction
3,3'-diamino-4,4'-azoxyfurazan (DAAF) is an energetic material that was first synthesized in 1981 [1]. It is part of a class of energetic materials that have high nitrogen content. Recently there has been an interest in the research and development of these high nitrogen energetic materials. When developing new energetic materials or working with existing ones, it is important to characterize their safety and relative sensitivity against various stimuli. Small-scale safety testing, which is used to characterize the sensitivity of energetic materials, was completed previously at LLNL on DAAF in 1997-98 (see Appendix A). We recently received an additional lot of DAAF and have completed small-scale safety testing and thermal analysis on it.

Experimental
The DAAF used for this work is LANL material provided by Scott Kinkead and David Chavez of LANL. It was received in April 2006 and has been assigned lot # DAAF 2006.

DAAF was evaluated for friction sensitivity using the Jules-Peters BAM machine [2], which measures how an explosive reacts to shear stress. A 5 mg sample is scraped by a ceramic knob dragged sideways on a ceramic plate by a load weight ranging from 0.5 kg to 36 kg. The relative frictional sensitivity is based on the largest load where less than two reactions occur after ten trials.

Impact sensitivity of DAAF was measured using the LLNL small-scale drop-hammer impact sensitivity test [3]. With this test, a 2.5 kg weight is dropped from different preset heights onto a 35 mg sample of explosive. Reaction or no reaction, which is based on the intensity of the sound emitted by the impact, is recorded. The impact sensitivity is

summarized as DH50, the height in centimeters where the probability of explosion is 50%.

The spark sensitivity test [4] was used to determine whether DAAF is sensitive to electrostatic discharge. With this test, a small sample of 3-5 mg is sealed in a plastic ring attached to a steel disk. A specified voltage is discharged through the sample. If no event is detected after ten trials, the explosive is designated as insensitive to spark. If an event is detected, the voltage level is lowered until 10 trials results in no events.

Differential Scanning Calorimetry (DSC) [5] was used to help determine the thermal properties of DAAF. DSC allows for the measurement of the difference in heat flow between the sample and an inert reference as a function of time and temperature. Observable thermal events that take place can be quantified and the onset of the decomposition exotherm can be used as an indication of thermal stability. During this test, a 0.5 mg sample is heated at a linear heating rate using a closed pan. DAAF samples were run at 1ºC/min and 10ºC/min at atmospheric pressure as well as 1ºC/min at 1000 psi.

The Chemical Reactivity Test (CRT) [6] is a method for characterizing the thermal stability of DAAF. Using a sealed stainless steel container in a silicone oil bath, a 0.25 g sample of DAAF is heated to 120ºC for 22 hours under 1 atm of He. The total gases evolved, including N_2, O_2, CO, NO, CO_2, and N_2O, are measured. Total gas evolution of more than 4 cc/g at 120ºC is considered suspect and additional testing must be done to determine its thermal stability. The CRT can also be used for short term compatibility evaluations by heating a mixture of explosive and the material being tested. The gas evolved from the mixture can then be compared to the gas evolved from the individual components to determine whether excess gas is evolved from the mixture, an indication of incompatibility.

The one-dimensional-time-to-explosion (ODTX) apparatus [7] was used to help determine the thermal sensitivity of DAAF. Using the ODTX apparatus, a 12.7 mm diameter pressed sphere, initially at room temperature, is inserted into a heated isothermal sample holder under confinement (150 MPa). The sample holder is made up of a pair of anvils, each with a hemispherical cavity, 12.7 mm in diameter. The time to explosion is the elapsed time between insertion of the sample and rupture of the containment. The time to explosion is recorded based on the loud noise produced by the explosion. The test is repeated over a wide range of temperatures.

Results and Discussion

Small-scale safety tests were completed on DAAF to characterize its relative sensitivity. In the friction sensitivity test, DAAF showed no reaction (0/10 Goes) at 36 kg, which supports that it is not sensitive to friction. In the spark sensitivity test, no reaction (0/10) was observed at 1 J, showing no observable sensitivity to spark. Table 1 shows the results for small-scale drop hammer impact sensitivity tests completed on DAAF along with typical values for other common explosives [8]. DAAF has impact sensitivity approaching that of TATB.

Table 1. Small-scale drop hammer tests for DAAF and other common explosives

Explosives	Dh50 (cm)
DAAF	158
HMX	29-35
RDX	28-37
Comp B	47-79
TATB	>177
PETN	10-22

Thermal sensitivity is also of critical importance for establishing the safety characteristics of explosives. The thermal sensitivity of DAAF is characterized using multiple tests including the CRT, DSC, and the ODTX apparatus. The CRT is useful for evaluating whether gases are produced at elevated temperatures over a designated time period. CRT data for DAAF show an average of 0.42 cc gas evolved per gram of material at 120ºC over 22 hours. An explosive with this value is considered thermally stable since the value is below 4 cc/g. Typical average gas evolution values for pure explosives are shown in Table 2. [8] The gas evolution from DAAF is somewhat higher than the nitramines and nitroaromatics in Table 2, and slightly lower than the nitrate ester.

Table 2. CRT values for DAAF and other common explosives at 120°C over 22 hours

Explosives	Average gas evolved cc/g
DAAF	0.42
RDX	0.18
HMX	0.12
TNT	0.16
TATB	0.12
PETN	0.59

DSC data can be used as an indication of thermal stability. DSC analysis on DAAF was done at two different heating rates, 1ºC/Min and 10ºC/Min. Figure 1 shows an overlay of the DSC profiles for DAAF at these heating rates. The difference in heat flow between the two profiles is due to the difference in heating rates. The total heat released is similar at both heating rates with values of 2727 J/g and 2378 J/g at 10ºC/min and 1ºC/min respectively. The onset decomposition temperature for DAAF material heated at 1ºC/min is 247ºC and the peak decomposition temperature is 248ºC. The onset decomposition temperature for DAAF material heated at 10ºC/min is 256ºC and the peak decomposition temperature is 266ºC. There is also a melt endotherm for DAAF heated at 10ºC/min that was observed at a peak temperature of 256ºC with the onset of the melt endotherm occurring at 254ºC. The melt endotherm is not observed at the slower 1ºC/min heat ramp rate due to a shift in the onset of decomposition to a lower temperature than its melt temperature. High pressure DSC that was also completed on DAAF at 1000 psi is shown

in figure 2. High pressure DSC data are similar to atmospheric pressure DSC data, which suggests that the thermal decomposition of DAAF does not depend on pressure.

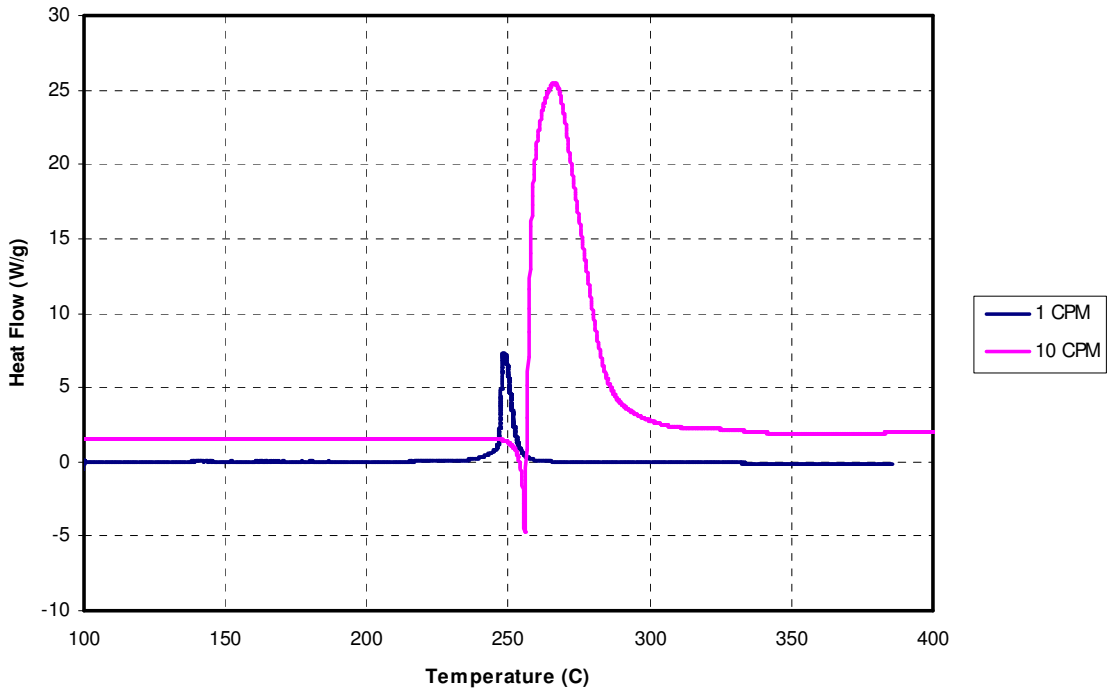

Figure 1. DSC profiles for DAAF at 1ºC/Min and 10Cº/Min heat ramp rates

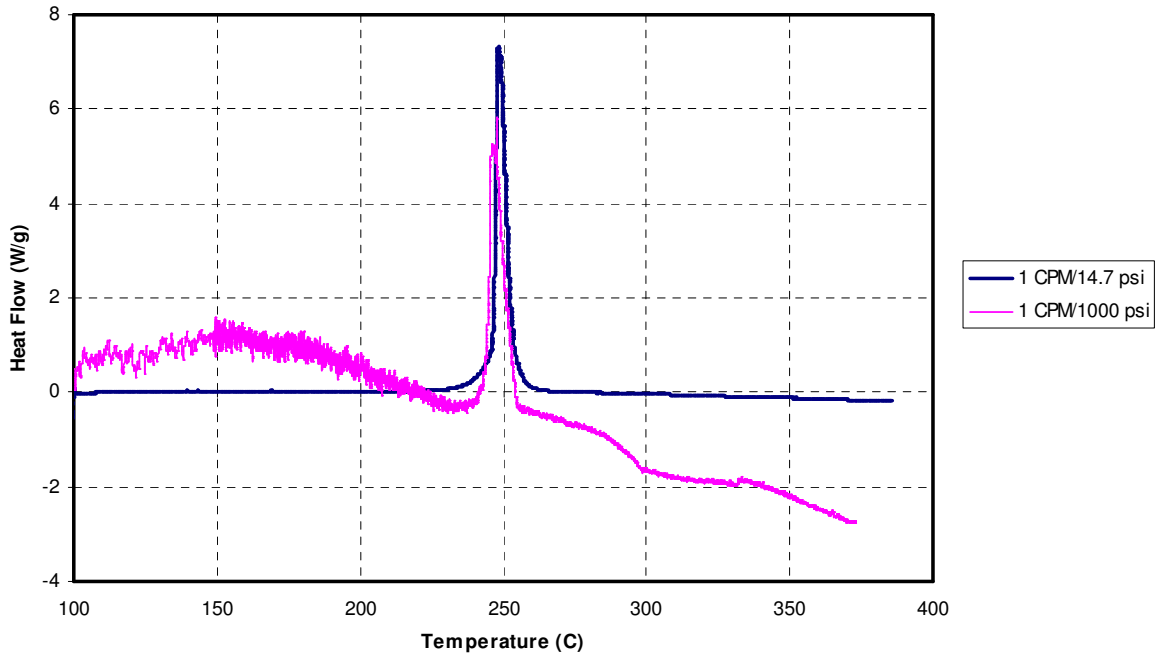

Figure 2. DSC profiles for DAAF at 1000 psi
compared with DAAF at atmospheric pressure

ODTX data show the relative thermal stability of a material under confinement over a wide range of well defined temperatures. For this test, DAAF was pressed into spheres with an average density of 1.68g/cc. During pressing, some of the DAAF spheres broke in half along the equator. The spheres that remained whole had some loose DAAF powder around the equator from the pressing.

The whole spheres were used first for ODTX experiments. ODTX experiments were successfully completed on whole spheres with the following temperatures as shown in Figure 5: 220ºC, 240ºC, and 260ºC. However, a premature reaction was observed for DAAF at 220ºC the first time it was run at this temperature. This may have been due to powder along the sphere equator coming off during insertion of the sphere into the sample holder and reacting early. Another premature reaction may have also been observed at 280ºC. However, at high enough temperatures, all times to explosion will be short, approximately two seconds or less, which is the time it takes for the sample to be inserted into the heated sample holder. Therefore, it is difficult to distinguish whether the DAAF run at 280ºC was indeed a premature reaction. Due to the limited amount of material available, ODTX was not rerun at 280ºC.

More ODTX experiments were completed using the DAAF spheres that broke in half during pressing. In these experiments, the sphere is remotely inserted into the sample holder, which means it can not be composed of two pieces. Therefore, a means to keep the sphere in one piece needed to be developed for the broken spheres. Two approaches were evaluated for using the broken spheres. The first approach was to glue the broken sphere back together. Three different adhesive systems were evaluated. The first adhesive evaluated was Permabond 910, which is a cyanoacrylate. Chemical reactivity tests were completed on DAAF and Permabond 910 to confirm that the materials are compatible prior to gluing the sphere back together. Based on the CRT results, there was no significant incremental gas evolved from the mixture compared to the individual components at 120ºC, indicating that DAAF and Permabond are compatible. Permabond 910 was used to glue the broken sphere along the plane where it had broken.

To determine the effect of gluing the hemispheres together, a second ODTX experiment at 220ºC was completed. DAAF hemispheres glued together reacted 20% faster than whole DAAF spheres. A reproducibility study has not been completed for DAAF, but based on reproducibility studies completed on other energetic materials, a 20% difference is probably significant. The presence of the adhesive is likely the cause of this difference. DSC that was completed on a mixture of DAAF and Permabond 910 confirms this. The onset of decomposition for the mixture is more than 30ºC lower than the onset of decomposition for DAAF alone.

Two more adhesive systems were evaluated. Halthane 88-2, which is a two-part elastomeric polyurethane adhesive that has a higher viscosity than Permabond 910 was evaluated as an adhesive to glue the hemispheres together along the perimeter. Prior to using Halthane for ODTX testing, Halthane was tested for compatibility with DAAF using both the CRT and DSC. Combining DAAF with Halthane gave similar CRT and DSC results as seen with combining DAAF and permabond 910. The onset of

decomposition of DAAF was again reduced by more than 30ºC. One more adhesive system was evaluated with DAAF. DER 332, an epoxy resin, was combined with Jeffamine T-403, an amine curing agent at a ratio of 100 to 47 respectively. 5-10% Cab-O-Sil was also included in the adhesive system to increase the viscosity. Again, this adhesive system combined with DAAF reduced the onset decomposition temperature of the DAAF substantially. ODTX experiments were not run on the second two adhesive systems due to high reactivity shown by the DSC results. Figure 3 shows the DSC profiles of DAAF with various adhesives. Table 3 summarizes the compatibility results of DAAF with the various adhesives. These results suggest that DAAF/adhesive compatibility is temperature dependent. At lower temperatures mixtures are compatible, but at higher temperatures, the onset of decomposition is reduced substantially.

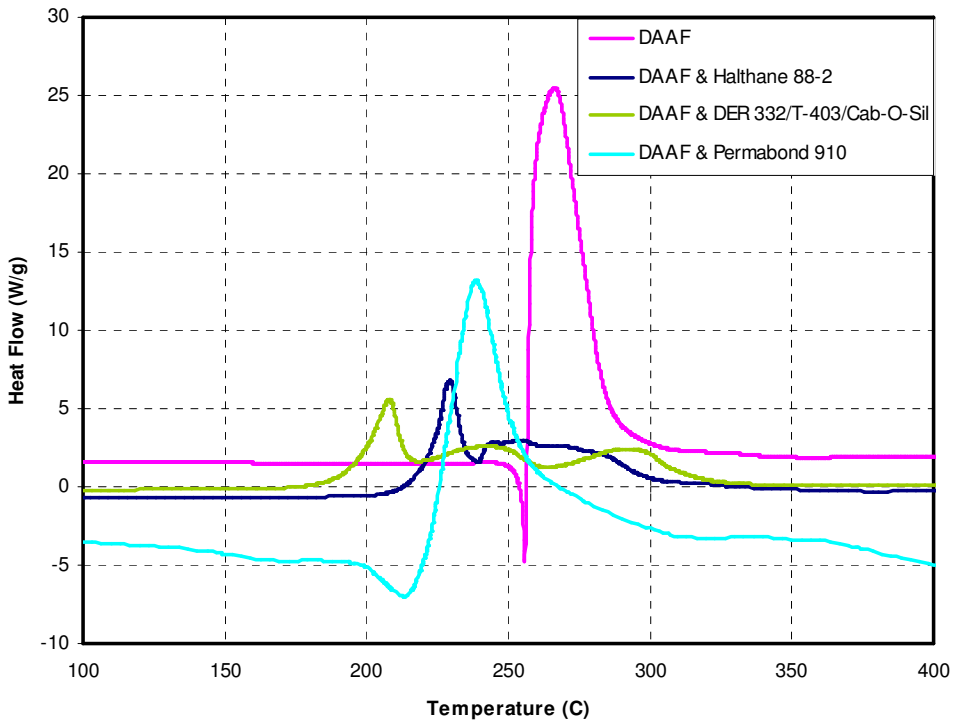

Figure 3. DSC profiles for DAAF and various adhesives at 10Cº/Min heat ramp rates

Table 3. DSC and CRT data for DAAF with various adhesive systems

Material	CRT at 120ºC Total gas cc/g (excess gas cc/g EX)	DSC Onset Temperature ºC
DAAF	0.42	256
Permabond 910	0.25	--
DAAF & Permabond 910	0.81 (0.14)	222
Halthane 88-2	0.07	--
DAAF & Halthane 88-2	0.73 (0.24)	222
DAAF & DER 332/T-403/Cab-O-Sil	Not tested	196

The second approach for using the broken spheres for ODTX was to place the broken sphere into an aluminum sample holder, which is typically used to hold liquid/paste explosives for ODTX experiments. In order to fit the DAAF sphere into the holder, the planes of the broken spheres had to be lapped. In addition, a section around the equator of the sphere halves was also lapped. An ODTX experiment was successfully completed on the DAAF placed in the aluminum sample holder at 210ºC. Although ODTX experiments were not repeated at the same temperature to compare the samples placed in an aluminum shell to the whole spheres, the sample run at 210ºC falls in line with the rest of the data. The validity of this method is also supported by fact that the time it takes to heat the aluminum shell is negligible compared to the length of the experiment.

ODTX tests were completed on DAAF at low temperatures which did not produce a violent reaction. A DAAF sphere that was heated at 200ºC did not react violently after seven days of heating. After 7 days the sample was cooled. Figure 4 shows a picture of DAAF after the sample was cooled along with DAAF powder for comparison. After the sample was cooled, the unconfined sample was reheated to 300ºC. It did not appear to react at this temperature. Other DAAF samples that were heated to 200ºC for shorter durations and did not react, reacted when ramped to 250ºC unconfined. At 200ºC DAAF may have decomposed slowly over the 7 day period while not violently rupturing the confinement, leaving a less sensitive residue behind.

ODTX data for DAAF are shown in Figure 5 along with data for HMX, TNT, TATB, and PETN for comparison. The ODTX values for DAAF are also listed in Table 4. DAAF ODTX data are similar to HMX and TNT, which indicates that its thermal sensitivity under the ODTX conditions is also similar to HMX and TNT.

Figure 4. *Left:* DAAF powder; *Right:* DAAF after 7 days of heating in the ODTX apparatus

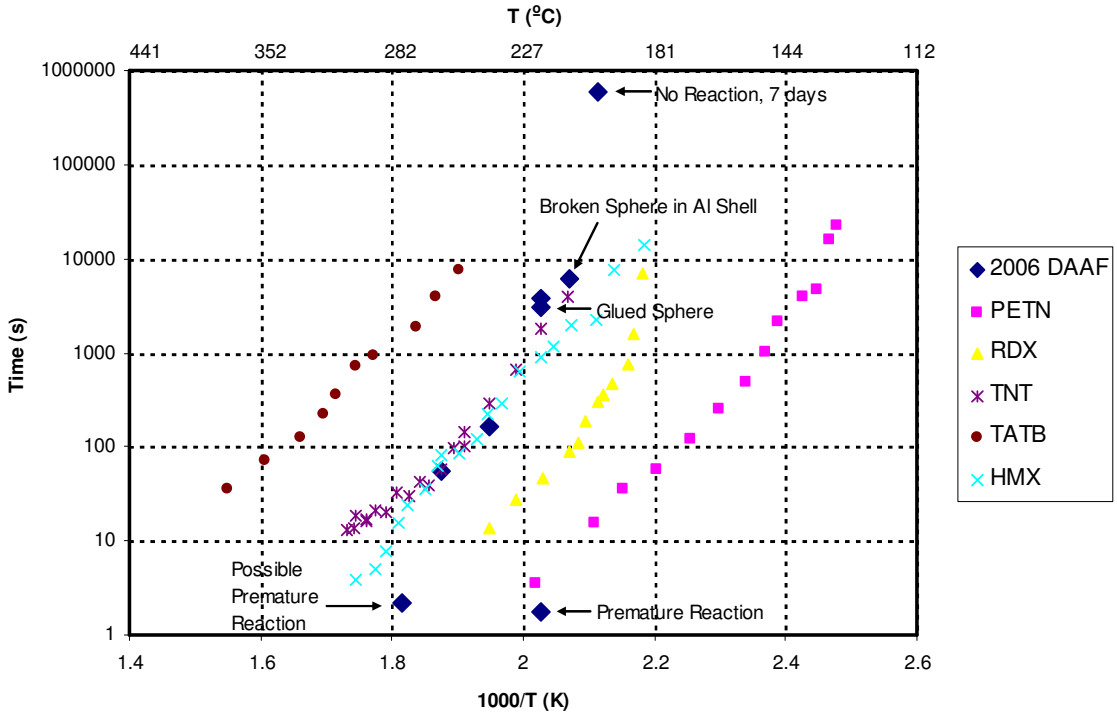

Figure 5. ODTX comparing DAAF to PETN, RDX, TNT, HMX, and TATB

Table 4. DAAF ODTX data

Temperature (°C)	Time (seconds)	Comments
200	603208	No reaction, 7 days
210	6136	Broken Sphere in Al Shell
220	3746	--
220	3010	Glued Sphere
220	1.8	Premature Reaction
240	166	--
260	56	--
280	2.1	Possible Premature Reaction

Conclusions

Small-scale safety testing that was completed on DAAF shows that it is insensitive to friction and spark and relatively insensitive to impact when compared with other common energetic materials. ODTX experiments showed that its thermal sensitivity is similar to that of HMX and TNT.

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Appendix A

Comparison of DAAF 2006 to previous lots of DAAF

Small-scale safety testing was completed on DAAF in 1997-98. The two lots of material tested were provided by Mike Hiskey at LANL in 1997-98 (Lots C-222 and C-273). A useful comparison was found by evaluating recent small-scale data for DAAF against the data from 1997-98. Both the DAAF 2006 material and the DAAF from 1997-98 do not show sensitivity to friction based on the BAM test. DAAF 2006 and DAAF from 1997-98 also have similar observed sensitivity to impact as shown in drop hammer results of 158 cm and 141 cm respectively.

The two materials, however, behave quite differently under thermal insult. DAAF 2006 is more thermally stable than the DAAF tested in 1997-1998 as observed in data for CRT, DSC, and ODTX.

A CRT was completed on DAAF Lot C-222 in 1997. The material was heated to 80°C for 22 hours. Data from this test was compared to DAAF 2006 that was heated to a higher temperature, 120°C, for 22 hours. Table A-1 illustrates that DAAF 2006 averages 4.6 times less gas evolved at the higher temperature than DAAF Lot C-222 at the lower temperature. This data suggests that DAAF 2006 is more thermally stable than DAAF Lot C-222.

Table A-1. CRT data for DAAF C-222 compared to DAAF 2006

Material	**CRT Average Gases Evolved**								
	Temp (ºC)	**N_2**	**O_2**	**CO**	**NO**	**CO_2**	**N_2O**	**Total (cc per 0.25g)**	**Total (cc/g)**
DAAF C-222	**80**	0.28	0	0.013	0	0.17	0.023	0.486	**1.944**
DAAF 2006	**120**	0.0631	0	0	0.0020	0.0378	0.0028	0.1056	**0.4222**

DSC data, shown in figure A-1 also supports that DAAF 2006 is more thermally stable than the DAAF C-222. The onset of a small decomposition exotherm is observed at 154ºC for DAAF lot C-222 at a 10ºC/min heating rate. The onset of a second exotherm is also observed at 230°C. DAAF 2006 does not show any exotherms prior to melting with a similar heating rate. This may be because the two DAAF materials were processed differently. There may be a less stable contaminant in DAAF lot C-222 that is causing early decomposition. This may also be the reason for increased gas evolution during the CRT.

ODTX data confirms that DAAF 2006 is more thermally stable than DAAF from 1997-98. Figure A-2 shows data taken in 1997-98 compared to today's data for DAAF along with other common materials. DAAF from 1997-98 behaves similarly to PETN as opposed to DAAF 2006, which behaves similarly to HMX and TNT.

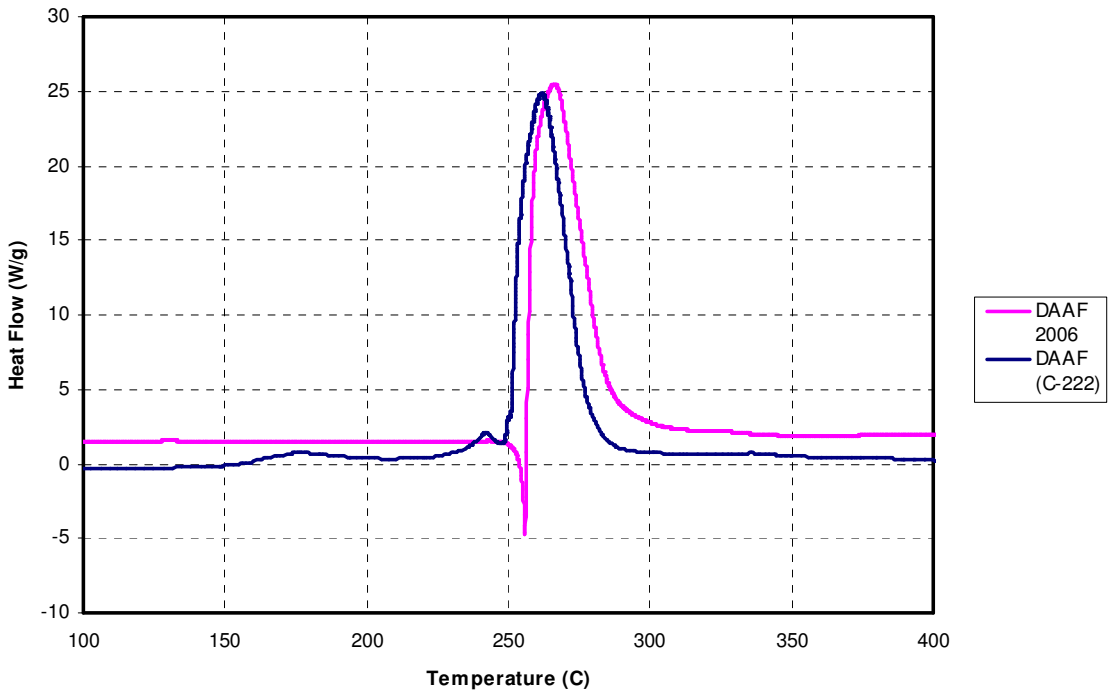

Figure A-1. DSC profiles for DAAF 2006 and DAAF C-222 at 10Cº/Min heat ramp rates

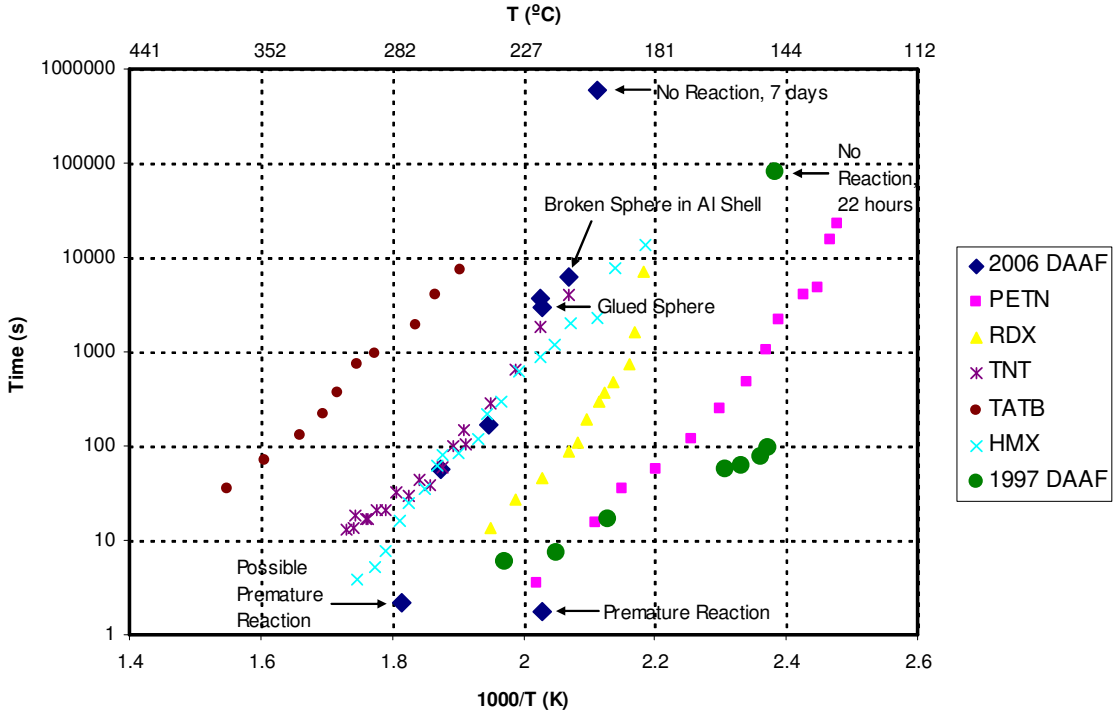

Figure A-2. ODTX comparing DAAF 2006 to DAAF from 1997-1998 along with other common explosives

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