CHARACTERIZATION OF THE UNCONFINED SLOW COOK-OFF RESPONSE OF NITRAMINES AND NITRAMINE COMPOSITES WITH TNT

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ABSTRACT

Due to the interest in developmental melt-castable explosive formulations devoid of TNT and the fact that both Composition B and Octol have relatively low self-heating temperatures in the one liter, spherical configuration, an accurate understanding of the thermal characteristics of these current TNT-based explosive formulations and their solid-state energetic components is warranted. The response of two different manufactures of RDX and their composites with TNT to relatively unconfined slow cook-off type conditions is hereby reported. The relevant testing procedure, designed to simulate worst-case melt kettle conditions, employs an open, one-liter Pyrex flask loaded with energetic material that is subjected to a linear thermal impetus following a prolonged isothermal hold. The safety oriented test experimentally determines the self-heating temperature associated with melt-castable and powdered explosives and the severity of the subsequent, unconfined catastrophic thermal decomposition reaction. Experimental results of nitramine and nitramine-TNT composites are characterized by two discernable self-heating processes, indicative of mechanistic changes associated with rapid decomposition rates. Reaction violence of nitramine composites and the source of the violence is detailed.

INTRODUCTION

The development of new explosive formulations encompasses a wide variety of techniques and disciplines ranging from small-scale sensitivity tests and analytical methods employing milligram quantities to full-scale explosive processing and subsequent testing using several hundred or thousands of pounds of energetic material. Paramount to this process is an accurate experimental determination of the energetic material’s response to thermal decomposition and subsequent validation of these experimentally determined values at processing/curing temperatures.

Using experimentally determined decomposition kinetics, overall heat of decomposition, density, heat capacity, and thermal conductivity (all values readily determined with analytical instrumentation), a sample’s internal temperature for a exothermic first-order decomposition reaction can be predicted for a specific geometry using the following equation:

\[-\lambda \nabla^2 T + \rho C_p \left(\frac{\partial T}{\partial t}\right) = \rho QZ e^{-E_a/RT}\]
where \( \lambda \) is thermal conductivity (cal K\(^{-1}\) cm\(^{-1}\) sec\(^{-1}\)), \( \nabla^2 \) is the Laplacian operator, \( T \) is temperature (K), \( \rho \) is density (g cm\(^{-3}\)), \( C_p \) is heat capacity at constant pressure (cal g\(^{-1}\) K\(^{-1}\)), \( Q \) is heat of decomposition (cal g\(^{-1}\)), \( E_a \) (cal mol\(^{-1}\)) and \( Z \) (sec\(^{-1}\)) are the activation energy and collisional density, respectively, from the Arrhenius equation and \( R \) is the ideal gas constant (1.987 cal mol\(^{-1}\) K\(^{-1}\)).

When the decomposition process produces heat faster than it can be dissipated to the surroundings, the energetic material will begin to self-heat and this will lead to a decomposition event that may be violent (rapid combustion) or catastrophic (explosion). Safe formulation and processing operations, coupled with storage and usage requirements, require that the energetic materials/formulations response to heat stimulus be known. Frank-Kamenetski\(\text{ii}^2\) and Chambr\(\text{e}^3\) have solved the above equation under the steady state condition \( \partial T / \partial t = 0 \), obtaining the following expression for critical temperature in terms of the related physical parameters:

\[
T_c = E_a/R \ln(a^2 \rho Q Z E_a/T_c^2 \lambda \delta R)
\]

where \( T_c \) is the critical temperature, \( a \) is a dimension (e.g., radius of a sphere or infinite cylinder or half thickness of an infinite slab), and \( \delta \) is a shape factor. The critical temperature is defined as the lowest constant surface temperature at which a material of a specific size, shape and composition can self-heat catastrophically. This latter equation, usually referred to as the Frank-Kamenetskii (F-K) equation, is solved by iteration and usually provides a conservative (worst-case) prediction of the \( T_c \) for operations in a melt kettle.

The analytical methodologies used to measure decomposition kinetics typically use between 200 and 500 \( \mu \)g of energetic material. Since such a small sample size is employed in these analytical methods, the onset of the self-heating process associated with a particular explosive occurs at temperatures far in excess of those at which self-heating would occur during the processing of large explosive batches or for full-scale munitions subjected to either a fuel fire or slow, prolonged heating during an accident. The relevant rate limiting mechanistic pathway of an overall decomposition process that is determined with use of analytical instrumentation on the small-scale is not necessarily the same rate limiting step at self-heating temperature for much larger samples, and hence may yield erroneous predictions of large-scale critical temperatures. Additionally, no information regarding reaction violence of the thermal event is provided by analytical instrumentation.

In order to obtain validation of predictions and gain insight about cook-off severity, a variety of mid-scale tests have been designed and implemented. The quantity of explosive utilized in these experiments can range from several grams to several kilograms, be either unconfined\(^4\), partial confined\(^5\), or heavily confined\(^6,7\), and may provide data such as temperature, time, pressure, kinetics, as well as overall reaction violence. A “One-Liter” test was developed at the Energetic Materials Branch of the Munitions Directorate, Air Force Research Laboratory, Eglin AFB, FL, to be used exclusively as a pre-scale-up safety characterization test for melt-castable formulations. The test essentially characterizes the entire self-heating process. This includes the
temperatures associated with the initiation of self-heating and determination of the temperature at which the final event occurs and insight into the severity of the thermal decomposition reaction under conditions that are similar to those associated with a melt-casting operation. Time-lapse video coverage of the experiment is recorded and often provides information about anomalies and changes observable in the recorded thermograms.

During the development of a series of melt-castable explosive formulations devoid of TNT, these non-TNT containing formulations were yielding self-heating temperatures significantly lower than was predicted. Since it was previously shown that Composition B had an exceeding low self-heating temperature, often processed above its self-heating temperature, and results in a violent final reaction, yet, it is safely processed in greater than 300-gallon melt kettles at a maximum temperature of 95°C, Composition B and its individual energetic components was subjected to one-liter cook-off testing. Investigations were continued and expanded to include TNT, regular RDX (HRDX), insensitive RDX, designated (IRDX) prepared in France by SNPE (Societe Nationale des Poudres et Explosifs), Composition B-3 prepared with IRDX, and ultimately a TNT/RDX (87/13) which at self-heating temperatures the RDX would be completely solublized in the TNT. Octol (75/25) and HMX powders were also investigated, but the endothermic β-HMX to δ-HMX phase change concurrent with the onset of self-heating made detailed analysis of self-heating in these systems difficult and will therefore not be reported here.

**ONE-LITER TEST SET-UP AND DATA ANALYSIS**

At the heart of one-liter test exists a one-liter, Pyrex, spherical, round bottom flask that has an approximate inside diameter of 12.4 cm. All experiments reported here were loaded incrementally using either chips or loose powder. Powdered explosives such as HRDX and IRDX used a 75/25 weight ratio of Class I and Class V, to increase overall bulk powder density. Melt-castable explosives, such as TNT and Composition B, were loaded leaving the meniscus of explosive approximately 1.0”-1.5” below the neck of the flask to allow expansion of the explosive at high temperatures.

A single use plywood oven is preconditioned at 110°C for 24 hours prior to use to remove volatiles from the plywood that would otherwise cloud the viewing glass. Following “bake-out” of the oven, two glass 0.375” thick panels, separated by 0.50” are inserted and used to view the flask during testing. The top of the oven is designed in two pieces to hold the lip of the flask securely, and flask is affixed with RTV. Two calibrated, Type-K thermocouples, encased in stainless steel shrouds are inserted, with one touching the bottom of the flask and the second positioned in the center. Two additional thermocouples are positioned freely inside the oven and used in the PID control loop that controls oven temperature. A four-element electrical resistive heater is used to heat the oven, and air is circulated by use of a small fan. A picture of the test set-up is provided in Figure 1. In some cases, a mirror positioned at approximately a 45° angle is placed to the side and back of
the flask to allow viewing of the backside of the flask.

Video of the test is recorded using a time-lapse video camera zoomed in such that the spherical flask fills most of the frame and a portion of the flask neck is visible. Five channels of thermocouple data are recorded once a minute (this includes the bottom and center thermocouples in the flask, two independent thermocouples inside the oven, and a thermocouple measuring ambient chamber temperature). Timestamp resolution is one hundredth of a second.

**Figure 1.** Picture of one-liter flask test setup.

The thermal protocol of the experiment involves an isothermal hold at 100°C for approximately six hours, to allow for a series of chip loads into the flask, melting and equilibration. Following the isothermal period, the oven is subjected to a linear ramp of 3.3°C/hr until cook-off of the explosive article.

Temperature-time data during the one-liter tests were recorded using a commercially available software program from Omega Engineering, Inc. The first five temperature data points, approximately five minutes of data, from the oven thermocouples were averaged. When the oven temperature exceeded this five-point average by one degree, the current timestamp in seconds is deducted from the experiment timing and yields a value of zero time for this temperature-time sample, indicating the experiment has started. This method ensures timing accuracy between experiments due to small differences in set-up time required to connect the heaters and safe the experiment following the start of data-logging.

Three temperature-time profiles are used during the analysis of the data. The first is a direct plot of the corrected time versus temperature for the oven and sample thermocouples. Data from four experiments, Composition B, Composition B-3 with IRDX, TNT, and TNT/RDX (87/13), is provided in Figure 2. The second profile, denoted as the “Delta Oven-Sample” plot, provides the corrected time versus the difference between the oven and sample thermocouples. This “Delta Oven-Sample” plot, detailed in Figure 3 for IRDX, shows the onset of self-heating as a downward trend following a plateau, where the sample and oven heating rates are roughly equivalent. In some cases, this plot also shows a downward discontinuity after a considerably long period of self-heating, indicating a mechanistic change in the decomposition reaction. In cases where a discontinuity in the “Delta Oven-Sample” plot is observed, the onset of self-heating is reported as the “non-catastrophic self-heating” (NCSH) and a downward discontinuity, if observed, is referred to as “catastrophic self-heating” (CSH). The last profile, denoted as the “Delta Delta” plot, detailed in Figure 4 using IRDX, provides the corrected time versus the derivative of the oven-sample
temperature difference. This “Delta Delta” plot is smoothed using a 20 to 60-point moving average in order to reduce experimental noise. The temperature and time associated with the onset of self-heating can then be readily determined by inspection of the plot. When the derivative of the oven-sample difference becomes negative (designated as point “A” on the plot), the sample is heating faster than the oven (i.e, NCSH). This method of determining the onset of self-heating generally provides detection of self-heating at earlier times and lower temperatures than visual methods relying upon raw data or oven-sample temperature difference. Subsequent testing has provided confirmation of the non-catastrophic nature of this temperature regime, where rapid cooling of the oven will provide enough thermal loss that the sample will cease self-heating. After the onset of self-heating, the sample continues to heat faster than the oven, however in most cases a discontinuity is visible, shown by point “B” in Figure 4, where the onset of “catastrophic self-heating” is readily observable.

Determination of final event temperature and time is provided by use of logic checks on the upward and downward slopes of the sample temperature. Typical slope limits employed are 10°C/min on the upward slope, to allow for high self-heating rates observed before final catastrophic events, and a 2°C/min temperature drop, to allow for thermocouple noise and for temperature fluctuations associated with sample bubbling during cook-off.

Figure 2. One-Liter Cook-off: Temperature vs. Time Profile of Melt-Castable Explosives Investigated

Figure 3. IRDX One-Liter Cook-off: Delta Oven-Sample Profile

Figure 4. IRDX One-Liter Cook-off: Delta Delta Profile

RESULTS AND DISCUSSION

A series of explosives were subjected to unconfined slow cook-off testing in the spherical one-liter geometry. Specifics of each test are reported, including the onset of non-catastrophic self-heating (NCSH), catastrophic self-heating (CSH), final event temperature, and
Table 1. Summary of Results for RDX, IRDX, TNT, and Binary Energetic Composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Test</th>
<th>Load &amp; Hold Time (min)</th>
<th>Non-Catastrophic Self-Heating</th>
<th>Catastrophic Self-Heating</th>
<th>Final Event</th>
<th>Severity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Time (min)</td>
<td>Temp (°C)</td>
<td>Temp (°C)</td>
<td>Time (min)</td>
</tr>
<tr>
<td>TNT</td>
<td>1-L</td>
<td>280</td>
<td>2569</td>
<td>211</td>
<td>227</td>
<td>2811</td>
</tr>
<tr>
<td>HRDX</td>
<td>1-L</td>
<td>320</td>
<td>1611</td>
<td>154</td>
<td>182</td>
<td>2028</td>
</tr>
<tr>
<td>IRDX</td>
<td>1-L</td>
<td>332</td>
<td>1763</td>
<td>167.5</td>
<td>187</td>
<td>2109</td>
</tr>
<tr>
<td>Comp B (HRDX)</td>
<td>RC\textsuperscript{2}1-L</td>
<td>391</td>
<td>1377</td>
<td>143</td>
<td>Oven heated to 156.7 °C @ 3.3 °C/hr then cooled to ~ 100 °C @ ~ 0.77 °C/hr. Sample &gt; self-heating temperature for 22.7 hrs</td>
<td>Cooled with oven</td>
</tr>
<tr>
<td></td>
<td>Iso\textsuperscript{3}1-L</td>
<td>480</td>
<td>Sample held at 133.3 °C for 20.1 hrs – liquid portion blackened but no evidence of self-heating</td>
<td>No self-heating</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Comp B-3 (IRDX)</td>
<td>1-L</td>
<td>644</td>
<td>1658</td>
<td>148</td>
<td>168</td>
<td>1866</td>
</tr>
<tr>
<td>TNT/RDX</td>
<td>1-L</td>
<td>528</td>
<td>1345</td>
<td>142</td>
<td>167</td>
<td>1793</td>
</tr>
</tbody>
</table>

(1) 13 % RDX by weight  
(2) RC = ramp and cool  
(3) Iso = isothermal  
(4) PD = partial detonation  
(5) D = detonation  
(6) E = explosion

**THERMAL PREDICTION VALIDATION**

Determination of the decomposition kinetics of TNT, HRDX, IRDX, and Comp B were performed using variable ramp rate differential scanning calorimetry and results are consistent with literature values, where available\textsuperscript{8}. The values are: TNT (E\textsubscript{a}: 29.01 kcal/mol, Z: 5.135x10\textsuperscript{8} Hz), HRDX (E\textsubscript{a}: 47.82 kcal/mol, Z: 3.31 x10\textsuperscript{18} Hz), IRDX (E\textsubscript{a}: 49.19 kcal/mol, Z: 1.47 x10\textsuperscript{19} Hz), and Comp B (E\textsubscript{a}: 38707 kcal/mol, Z:4.26 x10\textsuperscript{14} Hz). It is important to note that IRDX, which contains no traces of HMX, has essentially equivalent decomposition kinetics as HRDX. Prediction of the onset of NCSH by use of F-K scale-up equations yields values for these four explosives to be 160°C (TNT), 149°C (HRDX), and 150°C (IRDX), and 136°C (Comp B). The density parameters used to make predictions about HRDX and IRDX were the actual bulk densities in each experiment. Liquid densities of TNT and Comp B were lowered relative to literature Theoretical Maximum Densities (TMDs) by 11% of the TNT volume percentage. Thermal output parameters (Q) used were 300 cal/g (TNT), 500 cal/g (RDX), and 295 cal/g (Comp B).

Comparison of the NCSH temperature observed during the one-liter cook-off experiments relative to Frank-Kamenetskii scale-up equation
predictions showed the F-K predictions to be conservative in all cases (prediction is lower than actual). It was shown that HRDX and IRDX have measurably different NCSH temperatures even though predicted values were essentially identical. However, the self-heating temperature of TNT was approximately 50°C higher than predicted, indicating that either the decomposition kinetics measured by analytical instrumentation (measured between 270 and 325°C) are not accurate at cook-off temperatures and/or evaporation of TNT at these same temperatures provides a significant heat loss mechanism.

Neat TNT is thermally destabilized by the presence of RDX, be it either HRDX or IRDX, suggesting that the RDX is the thermal trigger in the thermal decomposition process associated with Comp B or Comp B-3. However, the decomposition of RDX in molten TNT does not account for the fact that Comp B and Comp B-3 NCSH temperatures are further reduced from neat RDX by another 10 to 15°C. If RDX was solely responsible for the observed self-heating in molten TNT/RDX mixtures, it is predicted that the self-heating temperatures would increase relative to neat RDX due to the lower heat of thermal decomposition (Q), approximated to zeroth order by the product of the neat Q and the weight fraction in the composite mixture.

As a result of this discrepancy and the known fact that RDX is soluble in TNT, a TNT/RDX composite was prepared using only enough RDX to be completely dissolved in molten TNT at the onset of self-heating in Comp B. Values of RDX solubility in TNT have been reported previously, however, the temperature ranges reported are all well below those needed for this study. As a result, literature RDX solubility vs. temperature data were extrapolated out to approximately 150°C. At this temperature it is expected that RDX’s solubility is approximately 16 weight percent. Since the exact solubility was in doubt a conservative value of 13 weight percent RDX was used to generate a composite with TNT. In order to expedite dissolution of RDX during cook-off testing, a milled RDX having an average particle size of 4 microns was used.

The temperature-time profile of the one-liter cook-off of TNT/RDX (87/13) is shown in Figure 2. The NCSH and CSH temperatures of the TNT/RDX (87/13) mixture are consistent with both Comp B and Comp B-3 (IRDX), and provides evidence that the thermal destabilization of such binary mixtures is related to the decomposition of solublized RDX in TNT. The final event temperature of the TNT/RDX (87/13) explosive formulation is in excess of 120°C higher than either Comp B or Comp B-3 (IRDX), and suggests that ignition/explosion during thermal runaway is related to unsolublized RDX.

Detailed analysis of RDX immediately prior to ignition/explosion during thermal runaway is given in Figure 5. A large increase in thermal decomposition is observed in the temperature-time trace at 2003 minutes into the experiment. Correlation of thermal behavior with videography suggests a mechanistic change in the decomposition pathway of RDX, with the generation of NOx being visible in the neck of the flask, immediately prior to melting. The sample temperature increases rapidly just when NOx becomes visible and a rapid temperature
increase is observed even while RDX is melting, even though melting is an endothermic event. The decrease in the rate of temperature rise, at point “C” in Figure 5, is associated with the forcing of RDX into the neck of the flask and an increase in the surface area by which heat can be liberated. Further oscillations in the thermal trace are difficult to correlate with videography as the high NOx concentration makes the flask nearly opaque. Final event occurs at 2028 minutes with the center thermocouple reporting 208°C.

The “Ramp and Cool” experiment is identical to the standard one-liter protocol, including a prolonged isothermal hold at 100°C followed by a linear heating rate of 3.3°C/hr. During this experiment, the oven was heated to 157°C and then allowed to cool at a rate of 0.77°C/hr. This procedure insured that the Comp B sample was well into the NCSH regime. Thermal history of the experiment is provided in Figure 6.

Analysis of the sample thermocouple trace confirms that the Comp B sample was in the NCSH regime as the sample temperature remained fairly constant even as the oven temperature was decreased. Standard tests determined NCSH of Comp B to start at 142 and 145°C. As the oven cooled, the sample maintained an average temperature of approximately 147°C, until 2743 minutes into the experiment when the sample ejected a large amount of explosive into the one-liter flask’s neck and onto the top of the oven. Subsequent cooling from the ejection of sample quenched the self-heating reaction and the sample cooled to 137°C in 2 minutes, below the critical temperature. After quenching of the self-sustaining decomposition reaction, the sample continued to cool at a rate equivalent to the oven’s rate.

FIGURE 5. Temperature-Time Profile of HRDX immediately before thermal event. A) 2004 minutes, 182.3°C. NOx observed in flask neck. B) 2006 minutes, 184.2°C. Onset of melting. C) 2009 minutes, 187.7°C. RDX being pushed into flask neck.

VALIDATING THE NCSH TEMPERATURE REGIME

Two experiments were performed to investigate the validity of self-heating regimes, which to this point have tacitly been labeled NCSH and CSH. Comp B made with HRDX was tested twice using standard procedures to establish self-heating temperatures (NCSH and CSH). Two additional experiments were then performed to study the NCSH regime. These tests are designated as “Ramp and Cool” and “Isothermal Hold”.

FIGURE 6. Temperature-Time Profile of the “Ramp and Cool” experiment with Comp B.
An isothermal experiment was also performed on Comp B, where the sample was heated to 133°C and held for 1206 minutes. Although the sample darkened, no evidence of self-heating was observed. The Comp B sample did decompose and bubble, but the rate was not sufficient to produce heat at a rate greater than thermal conduction and convection could dissipate. This data again is consistent with the previously determined self-heating temperature of Comp B in the one-liter spherical geometry.

All unconfined, spherical one-liter tests reported in this manuscript show NCSH and a second discontinuity in the oven-sample difference plot designated at CSH. While the “Ramp and Cool” and “Isothermal Hold” experiments validate a NCSH regime for Comp B, the CSH regime is less defined from a theoretical standpoint. From a purely physical model considering only heat generation based upon a first-order decomposition reaction (Arrhenius decomposition kinetics) and heat loss limited by thermal conductivity of the energetic material in question, no prediction of a second, unique self-heating regime, designated in this manuscript as CSH, can be made.

The onset of CSH in the three different systems reported here (neat TNT, neat RDX, and TNT/RDX mixtures) is unique between the different systems but consistent between duplicate experiments performed on the same system. The CSH is therefore most likely to be associated with a dramatic change in the mechanism of the decomposition pathway, due to a change in the rate-limiting step of the decomposition mechanism, where the discreet mechanistic steps have different temperature dependencies (e.g., the initial rate-limiting step has a higher energy of activation than subsequent mechanistic steps). Insight into CSH is not provided in small-scale analytical techniques and underscores the need for validation of decomposition kinetics and self-heating temperatures for sample sizes approaching those of either full-up munitions or large explosive batches. The lack of knowledge that a CSH regime even exists is of concern, as models based upon chemical kinetics that predict time-to-event are therefore inaccurate, with reaction occurring much sooner than predicted (yielding a more hazardous scenario).

REACTION VIOLENCE DURING UNCONFINED COOK-OFF

Up to this point, this report has been concerned primarily with validation of the Frank-Kamenetskii scale-up equations derived on the small scale with medium scale tests, analysis of the experimental thermograms, and discussion of NCSH as well as detailing a new temperature regime designated as CSH. However, equally important is the overall reaction violence during unconfined cook-off, where determinations of reaction severity are directly applicable to either explosive processing in large batches used during loading of full-scale warheads or munitions exposed to extreme temperatures where the warheads have been designed to vent at low pressures to minimize property damage or reduce lethality in accident scenarios. While a specific set of criteria for determination of reaction violence levels has not been establish for the unconfined one-liter slow cook-off test, such as those used in small-scale cook-off bombs\(^6\), the authors...
have tried to mimic the criteria as much as is possible with wooden ovens.

The final event violence of both HRDX and Composition B made with HRDX were exceedingly violent, with either partial detonation or detonation occurring. The results of these two tests completely destroyed the wooden ovens, with the wooden panels being splintered. The final event of the IRDX cook-off ejected molten RDX out of the flask, with subsequent ignition, however, the oven remained intact until slowly consumed by fire. TNT cook-off produced a mild explosion, with the oven panels being thrown apart and burnt, but not splintered. For TNT, it appears that the ignition point was near the top of the oven, possibly from ejected TNT being forced out of the one-liter flask during vigorous bubbling of the molten TNT, and ignition of the TNT or its vapors resulting from contact with electrical components (heaters and fans) on the oven. TNT/RDX (87/13) resulted in a reaction similar to neat TNT, with a series of material ejections and ignition of the energetic material outside the oven.

The results of these experiments provide insight into the ignition mechanism of the TNT/RDX mixtures. When comparing neat HRDX to neat IRDX, there exists a large difference in reaction violence. When RDX is complete solubilized, as in the case of TNT/RDX (87/13), the reaction is only a burn. While the cause of the difference reaction violence between the neat RDXs is not certain, TNT/RDX mixtures that have unsolubilized RDX, either solid crystalline or molten RDX, are exceedingly violent, yet neat IRDX just burns.

It is understood that RDX is soluble in TNT and a dynamic equilibrium would be expected to be established, where at equilibrium, the rate of RDX dissolution into TNT and precipitation from TNT is equal. This dynamic equilibrium in TNT systems may allow the conversion between relatively void free RDX crystals (IRDX) that when precipitated from TNT yields highly defected crystals. 

This hypothesis would account for the reaction violence in all experiments reported; differences in reaction violence between neat HRDX and IRDX, increased reaction violence of Comp B-3 made with IRDX relative to neat IRDX, and the decreased reaction violence of TNT/RDX (87/13) that was made with 4 micron HRDX relative to either neat HRDX or Comp B made with HRDX.

**SUMMARY**

A detailed description of an unconfined cook-off test at the one-liter scale, having a spherical geometry is reported for use with both melt-castable as well as powdered explosives. Data is reduced and plotted in two formats; a “Delta Oven-Sample” plot and a “Delta Delta” plot. Both plots are utilized to graphically determine two self-heating regimes designated as non-catastrophic self-heating (NCSH) and catastrophic self-heating (CSH). The NCSH regime occurs at lower temperatures than does CSH and denotes the onset of self-heating traditionally reported. The CSH regime, which is observable in all experiments report in this manuscript, corresponds to a mechanistic change in the decomposition pathway of the explosive at rapid decomposition and heat evolution rates. The mechanistic change is likely associated with a switch of rate-limiting steps in the overall
decomposition pathway, where an intermediate decomposition product may then be auto-catalytic with virgin explosive material.

TNT is thermally destabilized in the presence of RDX, and the onset of self-heating is related to the decomposition of solubilized RDX in molten TNT. However, the final event temperature and reaction severity associated with TNT/RDX composites is related to unsolubilized RDX immediately following melting.

High quality, relatively defect, void, and crack free crystals of RDX, designated as IRDX, during cook-off of neat IRDX produces a much more mild final event that more highly defected crystals of RDX (HRDX). However, when mixed with TNT, a dynamic solution equilibrium allows IRDX to enter molten TNT and then be re-precipitated as ill-defined crystals which undergo cook-off with a more violent final event. In the absence of RDX crystallites, as in the case of TNT/RDX (87/13), the cook-off event temperature is dramatically increased and reaction violence decreased.

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