
**Journal of Energetic Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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**To cite this Article** McKenney Jr., R. L. and Stevens, W. E.(2000) 'Binary phase diagram series: 1,3,3-trinitroazetidine (TNAZ)/1,3,5-trinitrobenzene (TNB)', Journal of Energetic Materials, 18: 4, 241 — 273
**To link to this Article: DOI:** 10.1080/07370650008219112
**URL:** http://dx.doi.org/10.1080/07370650008219112

# BINARY PHASE DIAGRAM SERIES: 1,3,3-TRINITROAZETIDINE (TNAZ)/1,3,5-TRINITROBENZENE (TNB)

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## ABSTRACT

The binary phase diagram for the 1,3,3-trinitroazetidine (**TNAZ**)/1,3,5-Trinitrobenzene (**TNB**) system has been predicted computationally and determined experimentally. Mixtures exhibit the thermal characteristics associated with a simple binary eutectic system affected by both non-ideal behavior of the two components and observable polymorphism associated only with **TNB**. Experimental eutectic temperature/composition (°C/mol percent **TNAZ**) values in the binary mixtures believed to contain one or more of the **TNB** polymorphic modifications, **I**, **III** and **IV**, are 68.4/53.4, 63.6/47.8 and 62.0/45.6, respectively.

Journal of Energetic Materials Vol. 18, 241-274 (2000)
Published in 2000 by Dowden, Brodman & Devine, Inc.

## INTRODUCTION

1,3,3-Trinitroazetidine (**TNAZ**) is a powerful and thermally stable energetic material with high volatility and a tendency to form low-density castings at atmospheric pressure[1]. Both characteristics are detrimental to melt casting operations with **TNAZ** and to the formation of usable explosive billets. **TNAZ** was first prepared by Archibald and co-workers in 1990[2] and has been investigated extensively at this laboratory. It was anticipated that these unacceptable characteristics could be tempered by forming binary eutectic compositions with other energetic materials. To date, **TNAZ** mixtures with pentaerythritol tetranitrate (**PETN**), 2,4,6-trinitrotoluene (**TNT**), 1,3,5-trinitrobenzene (**TNB**) and *N*-methyl-*p*-nitroaniline (**MNA**) have been characterized for explosive performance and thermal/shock sensitivity[3, 4, 5 and 6]. It has been demonstrated during a previous investigation[7] that **TNAZ** exists in at least two polymorphic modifications, one stable (**TNAZ I**) under ambient conditions and one unstable (**TNAZ II**), and that the former is more dense than the latter. Crystal density increases with the spontaneous transition from **TNAZ II** to **I** resulting in a dendritic structure with characteristic macro-shrinkage cracks. It is these cracks, distributed irregularly throughout a cast **TNAZ** billet, that are believed to be the primary cause of the observed low bulk density.

The **TNAZ/TNDAZ**[7], **TNAZ/TNT**[8] and **TNAZ/ADNAZ**[9] binary eutectic systems have been previously characterized by using differential scanning calorimetry (DSC) and hot stage microscopy (HSM).

## EXPERIMENTAL

### Phase Diagram Calculation

Liquidus temperatures associated with this binary eutectic system were computationally derived by solving equation (1),

$$R\ln x = \Delta H_{fus}(-1/T + 1/T_o) \qquad (1)$$

where T is the melting point (K) of the eutectic composition, $T_o$, $\Delta H_{fus}$ and x are the melting point (K), heat of fusion (cal $mol^{-1}$) and mol fraction of component A or B, respectively, and R is the gas constant (1.987 calories $K^{-1}$ $mol^{-1}$). Experimental melting points, determined by DSC heating operations on mixtures of the stable polymorphs of both components, were used for comparison with their corresponding calculated values.

### Thermal Characterization

a. Differential Scanning Calorimetry (DSC)

**TNB** and selected **TNAZ/TNB** mixtures were thermally characterized by using a TA Instruments Dual Differential Scanning Calorimeter, Model 912, equipped with a 2100 Thermal Analyzer Data System. **TNAZ** was previously characterized[7]. Standard aluminum sample pans and lids, TA Instruments Part Nos. 072492 and 073191, were used for all melting operations carried out by using the standard Dual Sample DSC (DSDSC) cell. Lids were inverted to minimize free volume over the sample. An upper temperature limit of 130 °C and a sample weight not exceeding 2.0 mg were used to minimize the possibility of leakage from the sample pans. All heating operations were started at 30 °C.

At least two melting operations were carried out on all mixtures at a heating rate of 1 °C/min. Special DSC experiments, where the melted sample was quenched in liquid nitrogen, were also carried out with neat **TNB** at a heating rate of 5 °C/min to search for polymorph modifications in a time-expedient manner. Cooling operations were either uncontrolled or accomplished at approximately 5 °C/min by using ice/water as a cooling medium. Peak temperatures are reported for all endothermic and exothermic processes. Mixtures were prepared by grinding weighed portions of dry energetic materials in an agate mortar with a glass pestle to ensure homogeneity. The DSC was calibrated by using indium metal as a temperature and calorimetric standard.

b. Hot Stage Microscopy (HSM)

HSM experiments were carried out by using a Mettler Hot Stage, Model FP 82, equipped with a FP 80 Central Processor. All observations were made with a Leitz Orthoplan Universal Largefield microscope equipped with a polarizing condenser and high-resolution video system, Javelin Smart Camera, Model JE3762DSP, which was operated at shutter speeds of 1/250 or 1/500 s. The video system is also equipped with a FOR-A video timer, Model VTG-55. All photomicrographs were obtained through a Leitz NPL 10X 0.20P lens (150x). Heating and cooling rates were 5 °C/min except below approximately 45 °C where the cooling rate is not controlled. The temperature at which the last crystal melts is reported as the liquidus temperature. A eutectic melting temperature, on the other hand, is reported as the temperature associated with the first indication of a melting process, generally crystal movement sometimes combined with readily observable liquid formation. The latter may be difficult to detect in mixtures with a high concentration of one component or the other. Solid state phase transitions are reported as a temperature range for slow processes and as a single temperature for fast processes.

Energetic Components

**TNAZ** was purified by crash-precipitation from a hot ethanol solution into ice and water and dried under vacuum. Analysis by high performance liquid chromatography showed **TNAZ** to be 97.8 percent pure. **TNB** was purchased from BOFORS Explosives (Sweden) and was reported to contain less than 2 percent impurities. Analysis by high performance liquid chromatography did not show the presence of impurities. The **TNB** was not subjected to further purification techniques.



## RESULTS

Thermal Characterization

a. Thermal Properties of TNB and TNAZ

The melting point and heat of fusion of **TNB I**, 123.1 ± 0.1 °C and 3.559 ± 0.023 kcal/mol, respectively (lit. mp 123-123.5 °C)[10, 11, 12], were obtained by DSC heating operations. Two polymorphic modifications, hereinafter referred to as **TNB III**, mp: 109.2 °C and heat of fusion: 3.097 ± 0.053 kcal/mol (lit. mp 109 °C)[11, 12] and **TNB IV**, mp 105.6 (lit. mp 106 °C)[10, 11], were observed during DSC heating operations. No heat of fusion was obtained for **TNB**

IV, since the endothermic event associated with its melting was only observed once and that in conjunction with the TNB III melting endotherm. Other polymorphs of TNB have been identified, TNB II (mp 110 °C)[11, 12] and TNB V (mp 88 °C)[11]. The melting point and heat of fusion observed for TNAZ were 99.7 ± 0.1 °C and 6.607 ± 0.079 kcal/mol, respectively[8,9].

TNB melting and recrystallization characteristics were also observed by HSM operations carried out at a heating rate of 5 °C/min. The initial melting operation was carried out on a hot plate, where the sample was heated to approximately 130 °C then crash-cooled on a cold aluminum plate to about 10 °C with a 3-minute hold. Upon reheating, a color change was observed over the temperature range 88.8-95.4 °C (average 92.1 °C) with melting occurring at 109.9 °C (TNB III). There was no apparent change in the macro-shrinkage crack structure during this color change event. This color change is shown in Figure 1. The thin liquid film was slow-cooled in the hot stage at about 5 °C/min. to 40 °C, then heated to melting at 123.5 °C (TNB I). Melting was preceded by a color change at approximately 111 °C (Figure 2). The latter was accompanied by the formation of macro-shrinkage cracks suggesting a density increase. The thin liquid film was crash-cooled to approximately 10 °C on a cold aluminum plate, then heated from 26 °C to melting at 123.6 °C. A rapid solid-state

phase transformation occurred at 59.8 °C (Figure 3), which was accompanied by the formation of macro-shrinkage cracks. A color-change was also observed over the temperature range 105-113 °C. Supercooling is a problem encountered with both components and with the mixtures, especially those near the eutectic compositions, during recrystallization operations.

In an attempt to minimize supercooling by providing crystallization sites, 1.45 percent by weight $Al_2O_3$ was added to pure TNB prior to a series of DSC heating operations. Ten of these operations were performed at a heating rate of 1 °C/min on the same sample. Four of the first five yielded single endothermic events at 123.3 °C (TNB I melting). The fourth, performed after the sample had been cooled slowly and stored at ambient temperature for 5 days, also yielded an additional weak endothermic event at 55.8 °C. This is believed to be associated with the same solid-state phase transformation that was observed by HSM at 59.8 °C and again at 55.5 °C on the mixed fusion slide. These latter two observations are discussed in Section e. The last five heating operations yielded single endothermic events at 109.2 °C that correspond to the melting of TNB III. No problems attributable to supercooling were encountered with these mixtures.

b. Calculated Phase Diagram

The calculated melting points and compositions of the eutectics with the **TNAZ/TNB I** and the **TNAZ/TNB III** binary systems are 72.0 and 65.5 °C and 48.8 and 40.6 mol percent **TNAZ**, respectively. The composition values and associated liquidus temperatures used to construct the calculated phase diagram are shown in Table 1.

c. DSC Characterization of TNAZ/TNB Mixtures

Initial melting operations, carried out on seventeen freshly ground mixtures of **TNAZ** and **TNB I** at a heating rate of 1 °C/min, yielded a consistent endothermic event at an average temperature of 69.0 ± 0.04 °C that is caused by eutectic melting. This eutectic is hereinafter designated Eutectic I.

1. Eutectic composition.

**TNAZ** liquidus temperatures form a convex-shaped curve that is positioned below that calculated (theoretical) by using equation (1), while those associated with **TNB I** are similarly convex-shaped, but fall above the calculated liquidus curve. The

experimental temperatures from melting operations on physical mixtures are shown in Table 2.

Table 1. Mol Percent TNAZ/Calculated Temperatures Used to Construct the TNAZ/TNB I, III Phase Diagram

| Mol Percent TNAZ | Temperature (°C) TNAZ/TNB I | TNAZ/TNB III |
|---|---|---|
| 0.0 | 123.1 | 108.8 |
| 2.2 | 121.2 | 106.7 |
| 5.5 | 118.2 | 103.6 |
| 8.25 | 115.7 | 100.9 |
| 11.0 | 113.1 | 98.2 |
| 13.7 | 110.6 | 95.5 |
| 15.0 | 109.3 | 94.2 |
| 21.7 | 102.8 | 87.2 |
| 27.0 | 97.3 | 81.4 |
| 37.4 | 85.9 | 69.5 |
| 40.1 | 82.8 | 66.2 |
| 40.6 | 82.1 | 65.5[1] |
| 40.7 | 82.0 | 65.6 |
| 41.2 | 81.4 | 66.1 |
| 42.5 | 79.9 | 67.1 |
| 47.5 | 73.7 | 71.1 |
| 48.8 | 72.0[1] | 72.0 |
| 48.9 | 72.1 | 72.1 |
| 50.5 | 73.2 | 73.2 |
| 52.6 | 74.7 | 74.7 |
| 54.0 | 75.7 | 75.7 |
| 57.6 | 78.1 | 78.1 |
| 60.1 | 79.6 | 79.6 |
| 62.5 | 81.1 | 81.1 |
| 76.9 | 89.1 | 89.1 |
| 86.3 | 93.7 | 93.7 |
| 90.9 | 95.8 | 95.8 |
| 95.5 | 97.9 | 97.9 |
| 100.0 | 99.8 | 99.8 |

Remelting of samples obtained by freezing of the molten mixtures from the initial DSC melting operations does not significantly affect the liquidus temperatures of the mixtures

rich in **TNB I** or in **TNAZ**. The eutectic melting temperature, however, was shifted to an average value of 68.4 ± 0.15 °C. Since this relatively small shift in the eutectic melting temperature (69.0 to 68.4 °C) is believed to be associated simply with the condition of the sample (physical mixture versus fused), the

Table 2. Endothermic Peak Temperatures for Initial DSC Melting Operations with **TNAZ/TNB I** Mixtures (1 °C/min)

| Mol Percent **TNAZ** | Temperature (°C) Eutectic **I** | **TNAZ** | **TNB I** |
|---|---|---|---|
| 0 | | | 123.1 |
| 5.5 | 69.0 | | 119.0 |
| 8.25 | 69.0 | | 117.4 |
| 11.0 | 69.0 | | 116.3 |
| 13.7 | 69.1 | | 114.5 |
| 21.7 | 69.0 | | 106.0 |
| 27.0 | 69.1 | | 104.4 |
| | | | 102.8 |
| 37.4 | 69.0 | | 90.9 |
| 42.5 | 69.0 | | 85.0 |
| 47.5 | 69.1 | | |
| 52.6 | 69.0 | | |
| 57.6 | 69.1 | | |
| 60.1 | 69.0 | 75.4 | |
| 62.5 | 69.0 | 75.6 | |
| 76.9 | 68.9 | 84.0 | |
| 86.3 | 68.7 | 91.6 | |
| 90.9 | 68.7 | 93.0 | |
| 95.5 | 68.6 | 96.8 | |
| 100.0 | | 99.8 | |

eutectic is still designated Eutectic I. The **TNB I** remelt liquidus temperatures form a convex-shaped curve that is positioned through those temperatures from the initial melting operations. The trendlines (both $R^2$s = 0.991) through the

combined liquidus temperatures from the initial and remelting operations for both **TNB I** and **TNAZ** cross at 53.4 mol percent **TNAZ** and 68.2 °C. During remelting operations, liquidus temperatures associated with **TNB III** and what is believed to be **TNB IV** were observed. As with the **TNB I** polymorph, the trendline ($R^2$ = 0.984) through the **TNB III** liquidus temperatures is convex-shaped and is positioned above the trendline through the calculated temperatures. It crosses the **TNAZ** trendline at 47.8 mol percent **TNAZ** and 64.0 °C. The average experimentally determined melting temperature believed to be associated with the **TNAZ/TNB III** eutectic composition, hereinafter designated Eutectic III, is 63.6 ± 0.07 °C. The convex-shaped trendline through the three liquidus temperatures believed to be associated with **TNB IV**, one of which is the melting temperature of pure **TNB IV**, crosses the **TNAZ** trendline at 45.6 mol percent **TNAZ** and 62.3 °C. The experimentally determined average melting temperature of this eutectic composition, Eutectic IV, is 62.1 ± 0.09 °C. The data from all DSC remelting operations are summarized in Table 3.

In addition to the endothermic events discussed above, remelting operations with mixtures, especially those with high concentrations of **TNB**, exhibited other very weak to moderate endothermic events that are believed to be associated with that particular component. Those in the temperature range 41 to 54 °C were generally observed as doublets, and are believed to be

associated with solid-state transformations (see Section d). Mixtures with concentrations of 5.5, 11.0 and 13.7 mol percent **TNAZ** also exhibited endothermic events, sometimes as doublets, in the 90-92 °C temperature range. These events were observed in fourteen of eighteen remelting operations where the endotherms associated with Eutectics III and IV both occurred during the same melting operation. In three of the remelting operations, it is believed the 62/63 endotherms were too weak for the endotherm in

Table 3. Endothermic Peak Temperatures Associated with Melting Processes for All DSC Remelting Operations with **TNAZ/TNB** Mixtures

| Mol Percent | Temperature (°C) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Eutectic | | | | | | |
| **TNAZ** | I | III | IV | **TNAZ** | **TNB I** | **TNB III** | **TNB IV** |
| 0 | | | | | 123.4 | 109.2 | 105.6 |
| 5.5 | | 63.6 | 62.0 | | 119.2 | 104.6 | 100.7 |
| 8.2 | 68.7 | 63.7 | 62.2 | | 117.4 | 103.2 | 98.6 |
| | | | | | | 101.4 | |
| 11.0 | 68.8 | 63.7 | 62.1 | | 115.7 | 102.2 | |
| | | | | | | 100.3 | |
| 13.7 | 68.8 | 63.8 | 62.2 | | 111.8 | 95.7 | |
| 21.7 | 68.7 | 63.6 | 62.2 | | 107.5 | 91.0 | |
| 27.0 | 68.7 | 63.5 | 61.4 | | 100.4 | 88.2 | |
| | | | | | | 84.2 | |
| 37.4 | 68.4 | 63.8 | | | 87.9 | 77.7 | |
| 42.5 | 68.9 | 63.8 | 62.2 | | 85.0 | 67.4 | |
| 47.5 | 68.8 | 63.9 | 62.2 | 63.6 | 73.8 | | |
| 52.6 | 68.9 | 64.0 | | 66.8 | | | |
| 57.6 | 68.8 | 63.6 | | 72.6/68.6 | | | |
| 60.1 | 68.7 | 63.7 | 62.2 | 75.4 | | | |
| 62.5 | 68.6 | 63.8 | | 76.4 | | | |
| 76.9 | 68.1 | | | 84.2 | | | |
| 86.3 | 67.8 | 63.2 | | 91.6 | | | |
| 90.9 | 67.5 | | 62.3 | 93.4 | | | |
| 95.5 | 66.8 | | | 96.9 | | | |
| 100.0 | | | | 99.8 | | | |

the 90-92 °C range to be observed. In another remelting operation, the peak occurred when only a very strong endotherm at 62.0 °C was observed. The complex nature of the DSC thermograms associated with mixtures with a high concentration of TNB is demonstrated by the thermogram overlay, compiled from initial and remelting operations on a single sample with 11.0 mol percent TNAZ, shown in Figure 4. These endothermic peaks, believed to be associated with phase transformations, are summarized in Table 4.



All molten compositions are affected by supercooling with those closer to the eutectic composition often requiring special techniques to effect crystallization. These include long waiting periods without special cooling procedures or quenching on a cold metal plate or in liquid nitrogen. The complete phase diagram, calculated and experimental, is shown in Figure 5.

d. HSM Characterization of TNAZ/TNB Fused Mixtures

HSM melting operations were carried out at a heating rate of 5 °C/min on thin crystalline films of fourteen mixtures that were prepared initially on a hot plate. The primary purpose of these HSM operations was to look for phase transformations at

Table 4. Endothermic Peak Temperatures Associated with Phase Transformations Observed During Remelting Operations with TNAZ/TNB Mixtures

| Mol Percent TNAZ | Temperature (°C) Solid-State Transitions | | | | | Other |
|---|---|---|---|---|---|---|
| 5.5 | | | 47.6 | 50.1 | 52.4 | 90.5 |
| 8.2 | | | 47.4 | 49.8 | 53.8 | |
| 11.0 | | | 47.3 | 49.7 | | 90.8 |
| 13.7 | | | 47.6 | 50.0 | | 91.0 |
| 21.7 | 41.5 | | 48.4 | 49.6 | 53.0 | |
| 27.0 | 41.1 | 43.2 | | | | |
| 37.4 | | | | | | |
| 42.5 | | | 48.8 | 51.8 | | |
| 47.5 | | | | | | |
| 52.6 | | | | | | |
| 57.6 | | | | | | |
| 60.1 | | | | | | |
| 62.5 | | | 47.2 | | | |

temperatures below 60 °C and in the 90-91 °C temperature range. The results are summarized in Table 5. Extreme supercooling, especially in those mixtures in close proximity to the eutectic composition, also hampered HSM cooling operations.

e. TNAZ/TNB Mixed Fusion

A mixed-fusion slide was prepared by a modification of the method described by McCrone[12]. TNB was applied to the slide first with coverslip and rapidly recrystallized on a cold aluminum plate. TNAZ was then melted on the slide and allowed to wick under the coverslip until contact was made with the leading edge

of the solidified **TNB**. The contact line between **TNB** (upper left) and **TNAZ** (bottom right), running diagonally from the upper right-

Table 5. Results from HSM Operations at 5 °C/min

| Mol Percent TNAZ | Eutectic | Phase Transformation | | TNAZ | TNB I | TNB III |
|---|---|---|---|---|---|---|
| 0 | | 92.1 | (color change) | | | 109.9 |
| 2.2 | | 42 | (solid state) | | 121.3 | |
| 5.5 | 65.1 | 46.4 | (solid state)[1] | | 119.1 | 105.1 |
| | | 84.1 | (color change) | | | |
| 21.7 | 70.4 | | | | 109.3 | 88-95[2] |
| 27.0 | 68.5 | | | | 107.3 | |
| 47.5 | 69.9 | | | | 84.8 | |
| 52.6 | 68.8 | | | | 73.5 | |
| 57.6 | 67.9 | | | 73.8 | | |
| 60.1 | 62.7 68.0 | | | 79.0 | | |
| 62.5 | 68.6 | | | 76.8 | | |
| 76.9 | 68.2 | 51-55 | (solid state) | 91.6 | | |
| 90.9 | 61.6 69.4 | | | 95.3 | | |
| 95.5 | 62.3 | | | 98.6 | | |

1. See Figure 6.
2. Observed as a color change.

hand to the lower left-hand corner, is shown in Figure 7. Shrinkage cracks are positioned randomly in both materials. The eutectic composition is indicated by the diagonally positioned dark line with a zone of mixing to its immediate right. Upon heating at 5 °C/min, a solid-state phase transformation moved diagonally from top-right to bottom-left through the **TNB** at 55.5 °C. It is shown as a color change from a greenish-gray to pink in a color version of Figure 8. The arrow on the left side of Figure 8a indicates the position of the leading edge of the front. The

front has moved across the entire section of **TNB** in Figure 8b. Other changes in the appearance (light gray areas indicated by arrows in Figure 9) of the **TNB** occur prior to the initiation of eutectic melting at 69.4 °C. The line of liquefied eutectic composition is also shown in Figure 9.

f. TNAZ Behavior in Binary Mixtures

**TNAZ** has now been characterized thermally in binary mixtures with 2,4,6-trinitrotoluene (**TNT**), *N*-acetyl-3,3-dinitroazetidine (**ADNAZ**), 1,3-dinitro-3-(1',3'-dinitroazetidin-3'-yl)azetidine (**TNDAZ**), *N*-nitroso-3,3-dinitroazetidine (**ONDNAZ**)[13], as well as 1,3,5-trinitrobenzene (**TNB**). As can be seen in Figure 10, **TNAZ** behaves similarly and non-ideally in binary mixtures with **TNT**, **ADNAZ** and **TNB** in that all of the liquidus temperatures are in close proximity to a single trendline ($R^2$=0.990) and all fall below the trendline positioned through the calculated liquidus temperatures. The liquidus temperatures from mixtures with **TNDAZ** and **ONDNAZ**, on the other hand, fall close to the trendline through the calculated liquidus temperatures.

## DISCUSSION

Three polymorphic modification of **TNB** were observed during multiple DSC heating operations with the neat compound: **TNB I** (mp 123.1 °C), **TNB III** (mp 109.2 °C) and **TNB IV** (mp 105.6 °C). Heats of fusion were obtained only for modifications **I** and **III**. It was previously shown that **TNAZ** exists in at least two polymorphic modifications, one stable (**TNAZ I**) and one unstable (**TNAZ II**).[7]



Problems associated with supercooling were minimized in special experiments by providing recrystallization sites in the form of $Al_2O_3$, 1.45 percent by weight. Ten DSC melting operations on the same sample yielded evidence of only two polymorphic modifications, **TNB I** in the first five and **TNB III** in the last five. In operation number 4, however, a low-intensity endothermic event was observed at 55.8 °C which is believed to correspond to the solid-state phase transitions observed previously at 59.8 °C and at 55.5 °C during HSM heating operations on neat **TNB** and on a **TNB/TNAZ** mixed fusion slide, respectively.

A single temperature-composition diagram showing three simple binary eutectics that are governed by **TNB** polymorphism and non-ideal behavior on the part of both components describes this system. The heats of fusion for two of the **TNB** polymorphic

modifications, I and III, were acquired by DSC melting operations thereby allowing the calculation of liquidus curves. In both cases, the experimental liquidus temperatures were positioned above the calculated curves. The experimental **TNAZ** liquidus temperatures were, on the other hand, positioned below the calculated curve. This combination had the affect of lowering the experimental eutectic melting temperatures from those calculated, as well as increasing the **TNAZ** concentrations in Eutectics I and III.

The melting temperature for Eutectic I shifted from an average value of 69.0 ± 0.04 (initial melting operation) to 68.4 ± 0.15 °C (remelting operations). This is believed to have resulted from operating on physical mixtures in the former case and fused mixtures in the latter. The crossing of the **TNB** I and **TNAZ** trendlines occurs at 68.2 °C and 53.4 mol percent **TNAZ** as opposed to the calculated eutectic melting temperature at 72.0 °C and 48.8 mol percent **TNAZ**. The average melting temperature for Eutectic III was 63.6 ± 0.04 °C. The **TNB III** and **TNAZ** trendlines cross at 64.0 °C and 47.8 mol percent **TNAZ**, while the calculated values were 65.5 °C and 40.6 mol percent **TNAZ**. The trendline for **TNB IV**, obtained from only three data points, crosses that of **TNAZ** at 62.3 °C and 45.6 mol percent **TNAZ**, while the average experimental value was 62.0 ± 0.1 °C. As can be seen from the above data, there is excellent agreement between the trendline crossing temperatures

and the experimentally acquired average eutectic melting temperatures for all three eutectic compositions (I, III and IV).

Multiple endothermic events occurred in the temperature range 41 to 54 °C with the majority of the events occurring at average temperatures of 47.8 and 50.0 °C. Other endothermic events occurred at an average temperature of 91.1 °C. The lower temperature events were also observed during HSM operations and are believed to be associated with solid-state phase transitions. The higher temperature event was not observed during HSM operations with mixtures. The available data does not allow us to further define these events.

The similarity of the non-ideal melting characteristics associated with **TNAZ**, when in binary mixtures with **TNT**, **ADNAZ** and **TNB**, is believed to be associated with component interaction. These interactions, affecting the **TNAZ** component in a similar manner, lower its apparent heat of fusion, thus resulting in experimental melting temperatures below those calculated from the heat of fusion associated with neat **TNAZ**. A best fit, linear trendline through these combined data points has an R-squared value of 0.990. A similar interaction with **TNAZ** is not observed in its binary mixtures with **ONDNAZ**[13] and **TNDAZ**. The **TNAZ** melting temperatures in binary mixtures with these latter two compounds

tends to follow the calculated **TNAZ** melting temperature curve fairly closely.

## CONCLUSIONS

A temperature/composition diagram for the **TNAZ/TNB** binary system has been predicted computationally by using measured heats of fusion and melting points obtained from the neat components. The experimental diagram is that expected from a simple binary eutectic system affected by both non-ideal behavior and polymorphism. The observable polymorphism was associated solely with the **TNB** component. Three polymorphic modifications were observed. **TNB I** and **TNB III** were thermally characterized in sufficient detail to allow computational predictions of mixture melting temperatures. The **TNB IV** liquidus curve was described by only three experimental melting temperatures. A trendline through these three melting temperatures intersected the trendline through the **TNAZ** liquidus temperatures at 62.3 °C. This closely matched the experimentally determined average melting temperature of a eutectic composition (62.0 °C) that was later designated Eutectic IV. The average melting temperatures for Eutectics I and III were 68.4 and 63.6 °C, respectively, while the temperatures associated with the crossings of the trendlines through the **TNB I** and **III** and **TNAZ** liquidus temperatures were 68.2 and 64.0 °C, respectively.

The mol percent **TNAZ** associated with Eutectics I, III and IV, obtained from trendline crossing points, were 53.4, 47.8 and 45.6, respectively. None of the well-characterized components, **TNB I**, **TNB III** and **TNAZ**, behaved ideally in that their liquidus temperatures were positioned above those calculated for the first two and below for the latter one. Solid-state transformations were observed for a number of mixtures, usually with high concentrations of **TNB**, by both DSC and HSM operations in the 41-54 °C temperature range. Other changes, also believed to be solid-state transformations, were observed in the temperature range 91 to 92 °C by only DSC heating operations. The **TNAZ/TNB** binary mixture was not considered for further characterization because of the complex thermal properties that were deemed inappropriate for munitions application.



## ACKNOWLEDGMENTS

We thank Dr. Howard H. Cady, Los Alamos National Laboratory (retired) for his unselfish discussions and sharing of expertise with regard to experimental technique and data interpretation.

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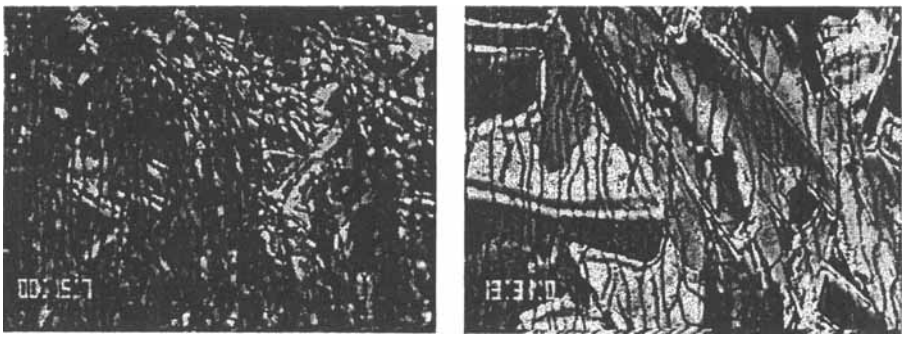
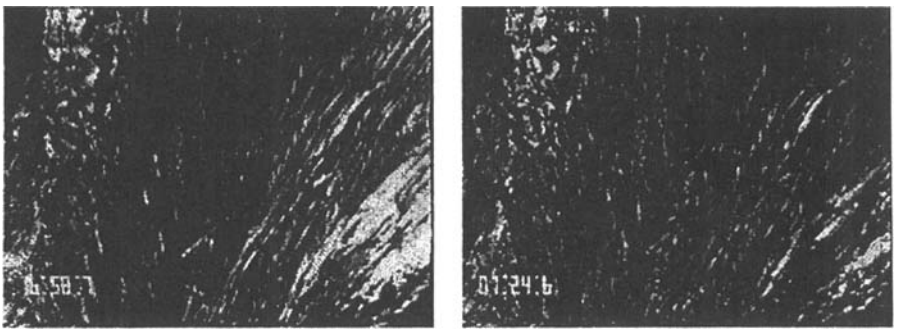


a b

FIGURE 1.

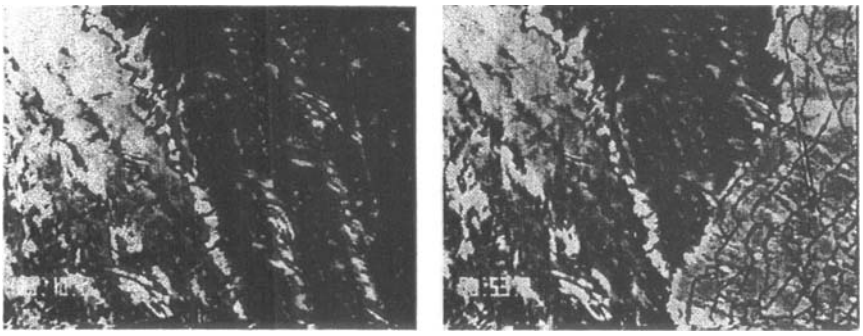
Color change associated with a solid-state phase transformation (88.8-95.4 °C) when a thin film of neat **TNB** was heated from 40 °C to melting at 109.9 °C (**TNB III**). (a) 40 °C, (b) 96 °C.



a b

FIGURE 2.

Color change associated with a solid-state phase transformation accompanied by the formation of macro-shrinkage cracks (approximately 111 °C) when a thin film of **TNB** was heated from 40 °C to melting at 123.5 °C (**TNB I**). (a) 40 °C, (b) ~111 °C.



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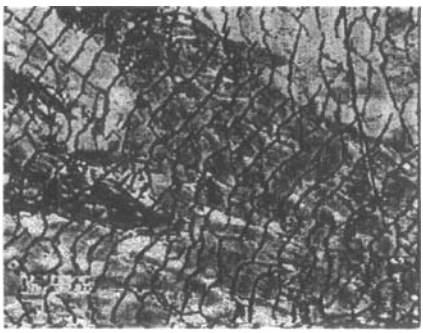


c

FIGURE 3.

**TNB** heated from 26 °C to melting at 123.6 °C (**TNB I**) after being crash-cooled from a previous melt on a cold aluminum plate. (a) 26 °C , (b) Solid-state phase transformation accompanied by macro-shrinkage cracks at 59.8 °C, and (c) 65 °C.

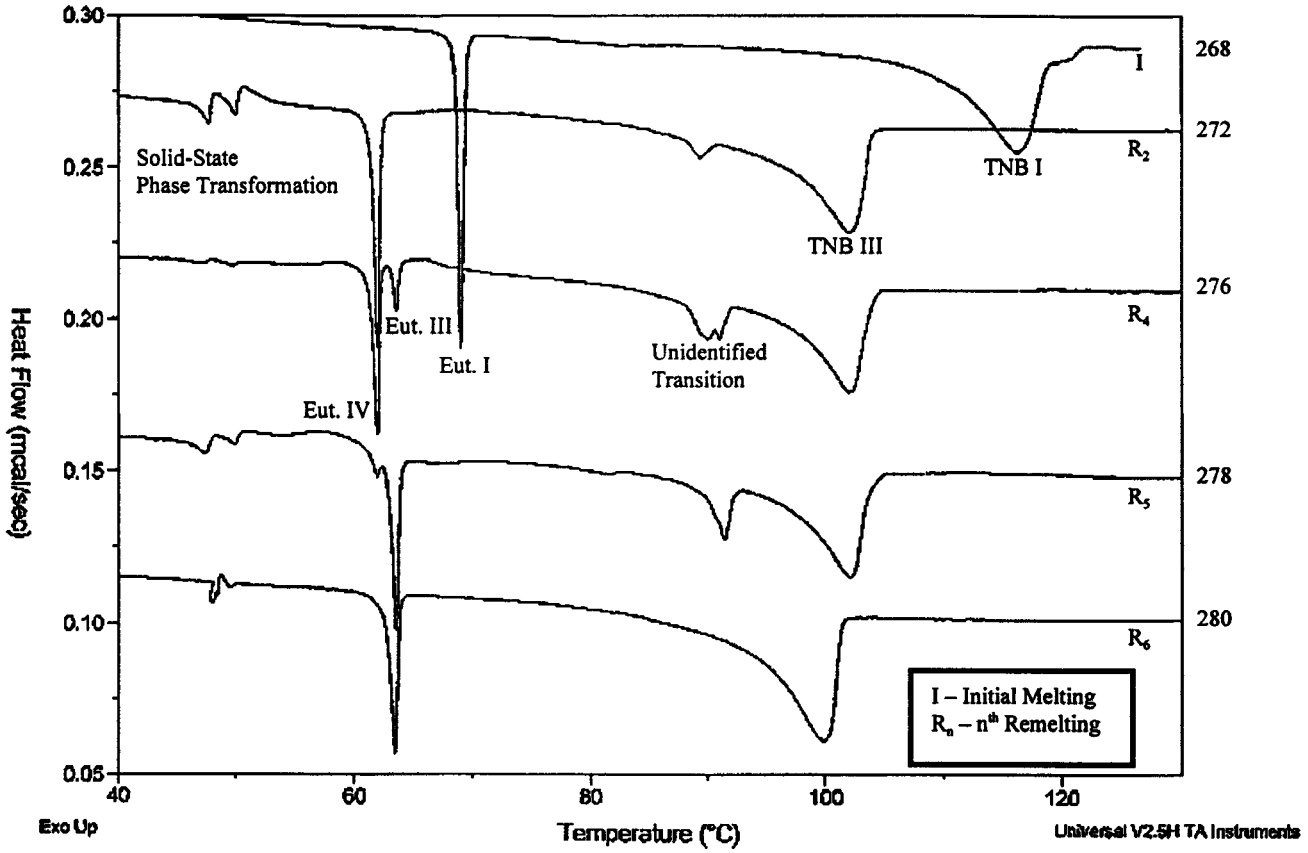



FIGURE 4.

Overlay showing the complexity of the DSC thermograms from the initial and subsequent reheatings of a **TNAZ/TNB** mixture containing 11 mol percent **TNAZ**.

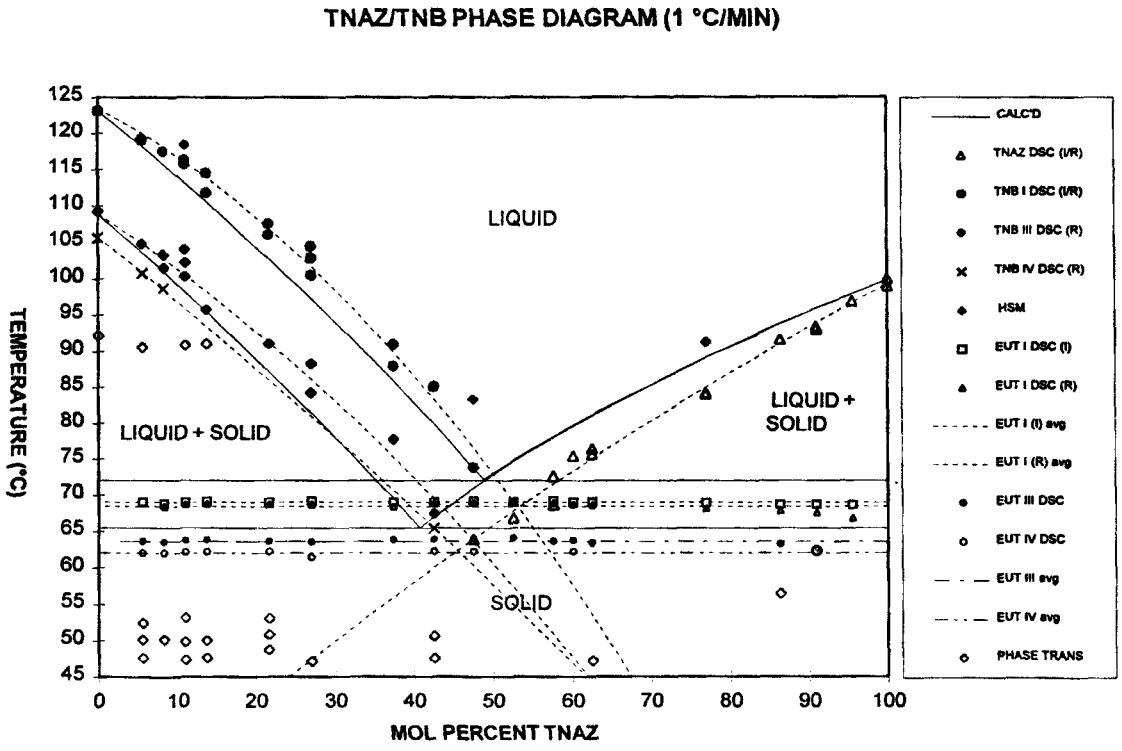
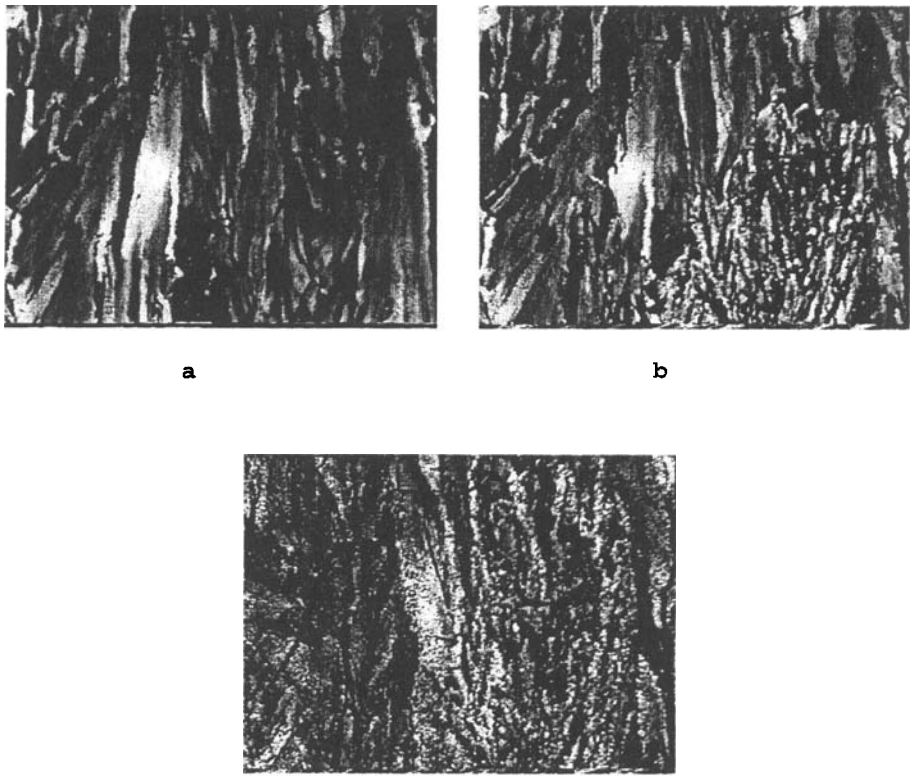



**FIGURE 5.**

Calculated temperature-composition diagram for the **TNAZ/TNB** system with experimental data from initial and remelting operations.



a b

c

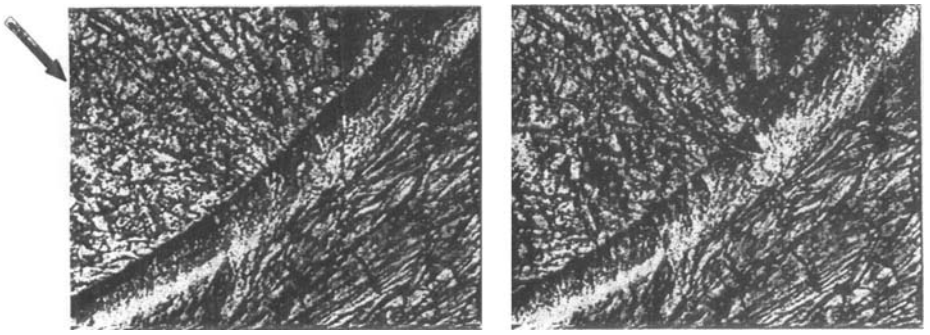
FIGURE 6.

Thin crystalline film of a **TNAZ/TNB** mixture containing 5.5 mol percent **TNAZ** showing a solid-state phase transformation moving from right to left. (a) 30 °C, (b) 46.4 °C and (c) 71.7 °C.

FIGURE 7.

Mixed fusion type thin crystalline film of the **TNAZ/TNB** eutectic system. **TNB** is shown in the upper left, **TNAZ** in the lower right and the eutectic region runs from the upper right to the lower left corner.





a b

FIGURE 8.

Mixed fusion type thin crystalline film of the **TNAZ/TNB** eutectic system showing a solid-state phase transformation. a) Arrow indicates position of the front moving from top to bottom across the **TNB** area at 55.5 °C. b) Phase transformation front has moved completely across the **TNB** (upper) thin film.

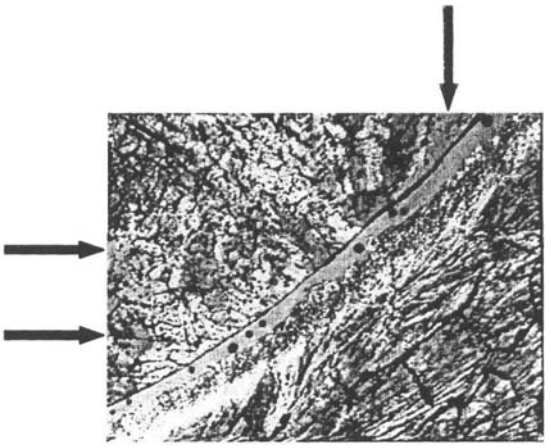


FIGURE 9.

Mixed fusion type thin crystalline film of the TNAZ/TNB eutectic system showing the beginning of the eutectic melt at 69.4 °C (pink area extending from the upper right to the lower left corner. Color changes occur in areas marked by arrows prior to eutectic wetting.

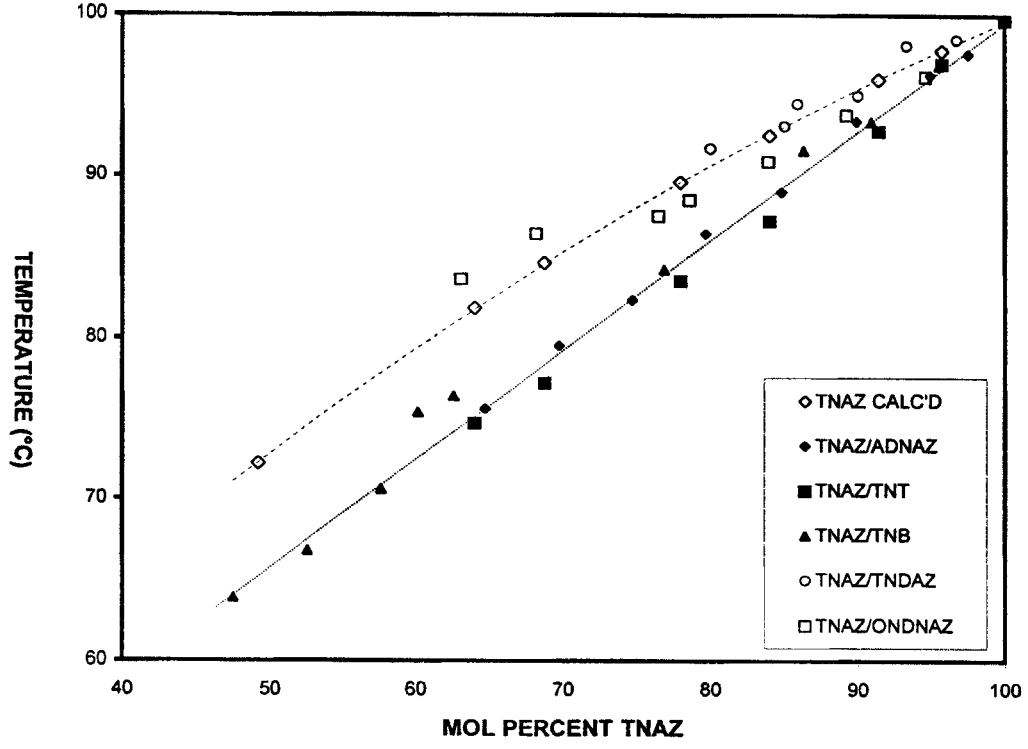



FIGURE 10.

Graphical representation of calculated and experimental **TNAZ** melting temperatures when in binary mixtures with **ADNAZ**, **TNT**, **TNB**, **TDNAZ** and **ONDNAZ**.