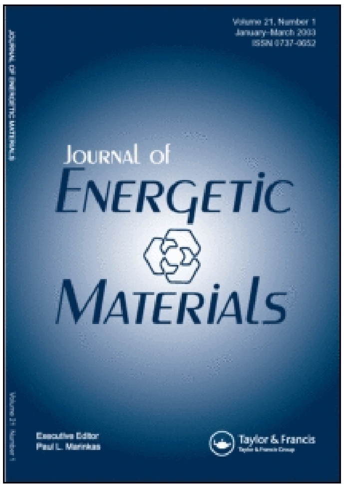

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Binary phase diagram series: 1,3,3-trinitroazetidine (TNAZ)/*N*-acetyl-3,3-dinitroazetidine[1] (ADNAZ)

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BINARY PHASE DIAGRAM SERIES: 1,3,3-TRINITROAZETIDINE (TNAZ)/*N*-ACETYL-3,3-DINITROAZETIDINE[1] (ADNAZ)

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ABSTRACT

Binary phase diagrams for the 1,3,3-trinitroazetidine (**TNAZ**)/*N*-Acetyl-3,3-dinitroazetidine (**ADNAZ**) system have been predicted computationally and determined experimentally. Physical mixtures exhibit the thermal characteristics associated with a simple binary eutectic system, while the behavior of fused mixtures is consistent with a simple linear solid solution system on the **ADNAZ**-rich side of the eutectic and a simple binary eutectic system on the **TNAZ** side. Experimental eutectic temperature/composition (°C/mol percent **TNAZ**) values for physical and fused mixtures are 75.4/63.8-64.9 and 74.2/61.7-64.0, respectively.

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INTRODUCTION

1,3,3-Trinitroazetidine (**TNAZ**), first prepared by Archibald and co-workers in 1990[2], is a powerful and thermally stable energetic material. Its high volatility and tendency to form low-density castings at atmospheric pressure[3] hamper melt casting operations with **TNAZ**. Researchers at this laboratory are attempting to both understand and temper these unacceptable characteristics 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[4, 5, 6 and 7]. It has been demonstrated during a previous investigation 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[8]. 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 immediate objective of this program is to experimentally characterize the **TNAZ/ADNAZ** binary eutectic system by using differential scanning calorimetry (DSC) supported by hot stage microscopy (HSM). The long-term objective is to generate a database of thermal characteristics and related properties obtained from a variety of promising binary, **TNAZ**-based systems and relate these findings to selected system shock sensitivities.

EXPERIMENTAL

Phase Diagram Calculation

The eutectic composition and melting temperature for this binary system were calculated by using a computer program in BASIC[9]. The program iteratively solves equation (1) by using component heats of fusion and melting points as input data,

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

where T is the melting point (degree K) of the eutectic composition, T_o, ΔH_{fus} and x are the melting point, heat of fusion 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 and heats of fusion, determined by DSC heating operations on mixtures of the stable polymorphs of both components, were used for comparison with their corresponding calculated values. Since the BASIC program does not provide a table of liquidus temperatures, they were computationally derived by solving equation (1) for the specific mol fraction values used during this investigation.

Thermal Characterization

a. Differential Scanning Calorimetry (DSC)

ADNAZ and selected **TNAZ/ADNAZ** 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[8]. 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 120 °C and a sample weight of 2.0 ± 0.1 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. DSC experiments were also carried out with neat **ADNAZ** 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 5 °C/min by using ice/water as a cooling medium. Peak temperatures are reported for all endothermic and/or 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 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 1 °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. Temperatures associated with eutectic or solid solution melting are differentiated from that of component melting by observing change in the rate of the melting process.

Energetic Components

ADNAZ and **TNAZ** were 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. No impurities were observed in the **ADNAZ** chromatogram.

RESULTS

Thermal Characterization

a. Thermal Properties of ADNAZ and TNAZ

The **ADNAZ** melting point and heat of fusion, 113.7 ± 0.06 °C and 6.130 ± 0.053 kcal/mol, respectively (lit. mp 111-112 °C[1]), were obtained by DSC heating operations. A polymorphic modification of **ADNAZ** (mp: 79.1 °C, heat of fusion: 4.721 kcal/mol) was observed during the fourth of seven DSC heating operations at 5 °C/min. The melting point and heat of fusion observed for **TNAZ** were 99.7 ± 0.1 °C and 6.607 ± 0.079 kcal/mol, respectively (lit. mp: 101.1 °C, heat of fusion: 6.405 kcal/mol[8]). **ADNAZ** melting and recrystallization characteristics were also observed by HSM operations where melting occurred at

114.4 °C. Supercooling is a problem encountered with both components during recrystallization operations. **ADNAZ** recrystallization, which occurred at 37 °C, is typically characterized by a formless crystal front with accompanying shrinkage cracks (Figure 1).

b. Calculated Phase Diagram

The calculated melting point and composition of the eutectic are 77.3 °C and 56.4 mol percent **TNAZ**, respectively. The composition values and associated liquidus temperatures used to construct the phase diagram are shown in Table 1.

c. DSC Characterization of **TNAZ/ADNAZ** Mixtures

Initial melting operations, carried out on twenty-one freshly ground mixtures of **TNAZ** and **ADNAZ**, yielded a consistent endothermic event at an average temperature of 75.4 ± 0.02 °C that is caused by eutectic melting. In order to determine the influence of heating rate on the eutectic melting temperature, variable heating rate experiments were carried out at 20, 10, 5 and 1 °C/min. These experiments yielded melting temperatures of 81.0, 78.8, 77.2 and 75.4 °C, respectively. Extrapolation of a trendline through these temperatures to zero heating rate afforded a minimum expected eutectic-melting temperature of 75.0

°C. This suggests DSC operations carried out at 1 °C/min are sufficiently slow for attaining equilibrium conditions. **TNAZ** liquidus temperatures form a convex-shaped curve that is positioned below that calculated (theoretical) by using equation (1). A trendline (R^2 = 0.992) through these data crosses the average eutectic melting temperature at 63.8 mol percent **TNAZ**. The position of the **ADNAZ** liquidus temperatures relative to its theoretical curve was less certain. To help establish the relative position of this curve, while also acquiring data at **TNAZ** concentrations above those resolvable by DSC operations, HSM experiments were carried out on mixtures with 52.1, 57.1 and 62.1 mol percent **TNAZ**. The observed **ADNAZ** melting temperatures were 86.3, 82.6 and 78.3 °C, respectively. These three data points were then incorporated into the overall graphical display as DSC data points. A convex-shaped trendline (R^2 = 0.986) through these combined data, which is positioned above the theoretical curve, crosses the average eutectic melting temperature at 64.9 mol percent **TNAZ**. These two trendlines intersect at 75.8 °C and 64.3 mol percent **TNAZ**.

Other endothermic events occur between those attributed to eutectic and **ADNAZ** melting. They fall into two data sets (A and B) that closely follow concentration-dependent trendlines (R^2 = 0.994 and 0.982, respectively). Data from all DSC melting operations on physical mixtures are shown in Table 2 along with both calculated and experimental heats of fusion. The calculated and experimental temperature/composition data are displayed graphically in Figure 2.

Table 1. Mol Percent/Calculated Temperatures Used to Construct the **TNAZ/ADNAZ** Phase Diagram

Mol Percent TNAZ	Temperature (°C)	Mol Percent TNAZ	Temperature (°C)
0	113.7	59.6	79.3
4.9	111.3	62.1	80.9
9.9	108.7	63.6	81.8
19.7	103.3	64.6	78.8
29.7	97.3	69.7	85.3
39.6	90.7	74.7	88.0
44.6	87.0	79.7	90.5
49.6	83.1	84.8	93.0
62.1	81.0	89.9	95.4
64.6	78.8	94.9	97.6
56.4	77.3	97.5	98.7
57.1	77.7	100.0	99.8
58.4	78.6		

1. Eutectic composition.

Remelting of samples obtained by freezing of the molten mixtures from the initial DSC melting operations significantly affected the thermal behavior of the mixtures rich in **ADNAZ**. Endothermic events associated with the **ADNAZ**-related melting processes form two diverging convex-shaped curves, the solidus (lower) and liquidus (upper). The solidus curve is continuous (without deflection) and detectable to 59.6 mol percent **TNAZ**. The **ADNAZ** liquidus temperatures are positioned slightly above the theoretical curve, while **TNAZ** liquidus temperatures are similar to those observed during initial melting operations.

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

Mol Percent **TNAZ**	Temperature (°C) Eutectic	B/A	**TNAZ**	**ADNAZ**	Hts of Fusion Calc'd/Found
0				113.7	6130
1				112.8	6135/6471
2.0		96.0/		112.8	6139/6196
4.9	74.2/77.4	94.3/104.0		111.2	6153/6204
9.9	75.1	91.4/100.6		108.6	6177/6123
19.7	75.6	89.9/95.2		104.2	6224/5631
29.7	75.5	/92.1		98.2/99.7	6271/5334
39.6	75.4	/86.0		90.4	6319/5744
44.6	75.4	81.3/83.1,84.8 86.7		88.7	6342/5265
49.6	75.4	/82.1		83.5	6366/5452
52.1	75.4	/79.8			6378/5685
54.6	75.4	/79.0			6390/5756
57.1	75.4				6402/5340
59.6	75.6				6414/5296
62.1	75.4				6426/5400
63.6	75.4				6433/5515
64.6	75.6		75.6		6438/5377
69.7	75.6		79.5		6462/5385
74.7	75.4		82.3		6486/6051
79.7	75.6		86.4		6510/5740
84.8	75.5		89.0		6534/6137
89.9	75.4		93.4		6559/6242
94.9	75.2		96.3		6582/6327
97.5	75.0		97.6		6595/6416
100.0			99.7		6607

Eutectic melting occurs at an average temperature of 74.2 ± 0.05 °C and is observed only at concentrations of 44.6 mol percent **TNAZ** and greater. Trendlines (R^2 = 0.9939 and 0.9905, respectively) through the **TNAZ** and **ADNAZ** liquidus temperatures cross the average eutectic melting temperature at 64.0 and 61.7 mol percent **TNAZ**, respectively, and intersect at 73.2 °C and 62.8 mol percent **TNAZ**.

All molten compositions were affected by supercooling. Those closer to the eutectic composition often required special techniques, either long waiting periods or quenching in liquid nitrogen, to initiate recrystallization. The data from all DSC remelting operations, including heats of fusion, are summarized in Table 3. Temperature/composition curves are shown in Figure 3.

d. HSM Characterization of **TNAZ/ADNAZ** Fused Mixtures

HSM melting operations were carried out on thin crystalline films of nine mixtures that were prepared on a hot plate. The average melting temperature for the eutectic composition was 74.5 ± 0.2 °C. As with DSC remelting operations, the **ADNAZ** solidus curve is continuous (without inflection) and was observed, usually as a color change, to 69.7 mol percent **TNAZ**. An example of a color change associated with the solidus curve is shown in Figure 4 for the composition containing 57.1 mol percent **TNAZ**. The **ADNAZ** liquidus temperatures were similar to those observed by DSC remelting operations.

Table 3. Endothermic Peak Temperatures for All DSC Remelting Operations with TNAZ/ADNAZ Mixtures

Mol Percent TNAZ	Temperature (°C) Eutectic	Misc	TNAZ	ADNAZ Liquidus	ADNAZ Solidus	Hts of Fusion
0				113.7	113.7	6130
4.9				111.0		6060
9.9				108.8	107.5	5777
19.7		90.0		104.7	98.5/99.2/100.9	5357
		94.2/96.1				
29.7		91.8/93.1		99.6	95.8	4981
39.6		85.1		91.2	87.2/82.7	5183
44.6	74.6			88.6	79.8	4275
49.6	73.8			83.2	76.4	4658
52.1	74.1			81.2	73.9	4248
54.6	74.2			78.8	71.0	4285
57.1	74.4			77.2	69.2	4336
59.6	74.4			76.6	66.9/68.0	4806
62.1	74.2					4548
63.6	74.6		NR[1]			5225
64.6	74.5		NR[1]			4862
69.7	74.3		78.3/79.5			5080
74.7	74.1		83.7			5069
79.7	74.0		86.2			5126
84.8	74.0		91.0			5802
89.9	74.2		93.7			5514
94.9	72.2		96.2			5825
97.5	73.6		97.5			5735
100.0			99.7			6607

1. Not resolved.

As with DSC cooling operations, HSM cooling operations were hampered by extreme supercooling, especially in close proximity to the eutectic composition. All temperatures from HSM remelting operations are shown in Table 4.

e. **TNAZ/ADNAZ Mixed Fusion**

A mixed-fusion slide was prepared by a modification of the method described by McCrone[10]. **ADNAZ** 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

Table 4. **TNAZ/ADNAZ** Data from All HSM Operations

Mol Percent TNAZ	Temperature (°C)				
			ADNAZ		
	Eutectic	TNAZ	Liquidus	Solidus	Misc
29.7			98.3/99.4	89.1/90.1	
39.6			92.8	82.1/85.1	
52.1			83.3	72.3/75.2	
57.1	74.3		79.4	70.3/67.8	
59.6	74.4		77.2	68.7	
63.6	74.2	76.7		60.4/63.4	
69.7	74.2	80.4		59.4	69.7[1]
74.7	74.5	84.2			
79.7	75.2	89.5			

1. Abrupt color change.

to wick under the coverslip until contact was made with the leading edge of the solidified **ADNAZ**. The horizontal contact line between **ADNAZ** (bottom) and **TNAZ** (top) is shown in (Figure 5). Shrinkage cracks in the **TNAZ** and **ADNAZ** thin films are positioned randomly and parallel to the contact line, respectively. No mixing or characteristic eutectic zones are apparent. Upon heating at 1 °C/min, melting initiated along the contact line at 72.6 °C forming a recognizable liquid channel by 73.9 °C (Figure 6).

During the subsequent cooling operation (1 °C/min), large platelets of **ADNAZ** grew across the liquid channel (Figure 7). Concurrent **TNAZ** crystal growth was not apparent. The residual liquid rapidly crystallized when the first **ADNAZ** platelet contacted **TNAZ** (Figure 8). There was no fine-grained crystal structure in the final solid to suggest the presence of eutectic mixture.

f. Solid-State Heat Treatment

Selected compositions were heat treated at 68-69 °C for varying time periods to induce solid-state transitions that may be detectable by subsequent DSC melting operations (initial). For example, samples of a mixture containing 19.7 mol percent **TNAZ** were heat treated for 120, 1140 and 7110 minutes. Each sample was then subjected to two consecutive DSC analyses at a heating rate of 5 °C/min. Concurrently, another sample of the same mixture was heat-treated for 1260 minutes by using the HSM, then heated at 1 °C/min through **ADNAZ** melting. This dual operation allowed us to observe the thermal behavior during the heat treatment period and during the subsequent heating operation. No melting was observed during the former operation. The above data are shown in Table 5.

Table 5. Melting Characteristics[1] of Heat-Treated Samples Containing 19.7 mol percent **TNAZ**

Expt.	Heat-Treatment		Temperature (°C)				
Type	Temp (°C)	Time (min)	Eut.	B	A[2]	Solidus[2]	Liquidus[2]
I[3]	none	none	77.2(s)	88.9(vw)			105.2(m)
I[4]	none	none	75.6(s)	89.9(m)	95.2(m)		104.2(s)
I	69	120	77.2(m)	91.7(br,m)			104.1(br,s)
I	68	1140		91.7(s)	98.6(s)		104.4(s)
I	68	7110			96.2(s)	100.8(s+)	104.2(s)
I[5]	68	1260		89.2[6]			106.2[7]
1R[8]	none	none				100.8(s)	104.5(s-)
1R	69	120				100.6(s)	104.5(m)
1R	68	1140				100.9(s)	104.4(s-)
1R	68	7110				100.5(s)	104.2(m)

Symbols = (s) strong, (m) medium, (vw) very weak, (br) broad, (+/-) more/less)

1. DSC experiments (5 °C/min) after heat-treatment.
2. **ADNAZ** events.
3. Initial melting operations.
4. DSC experiment (1 °C/min).
5. HSM experiment (1 °C/min) after heat-treatment.
6. First indication of melting.
7. Last crystal.
8. Remelting operations.

Samples containing 79.7 mol percent **TNAZ** were subjected to heat treatments at 65 and at 69 °C for 60 and 120 minutes, respectively. Initial DSC melting operations (5 °C/min) on both samples yielded average eutectic and **TNAZ** melting temperatures of 77.2 and 87.6 °C, respectively. The melting temperatures associated with these same two endothermic events from a non-heat treated sample were 77.5 and 87.0 °C, respectively. Remelting operations on the sample previously heat-treated at 69

°C for 120 minutes and on one that was not heat-treated yielded endothermic events at 75.2/87.1 and 75.3/87.4 °C, respectively.

DISCUSSION

Evidence of polymorphism was observed during multiple DSC heating operations (5 °C/min) on neat **ADNAZ**. A single endothermic event occurred at 79.1 °C during experiment number four of seven consecutive melting operations. The average melting temperature observed during the six other experiments was 113.7 ± 0.06 °C. This lower melting polymorph was not observed during DSC melting operations carried out at a heating rate of 1 °C/min on neat **ADNAZ**, on any mixtures or during HSM operations. It was previously demonstated[8] that **TNAZ** exists in at least two polymorphic modifications, one stable (**TNAZ I**) under ambient conditions and one unstable (**TNAZ II**). The transition from **TNAZ II** to **TNAZ I** was observed only during HSM recrystallization operations.

This binary system is described by two temperature-composition diagrams, a simple binary eutectic from melting operations on physical mixtures and a combination of a simple linear solid solution/simple binary eutectic from remelting operations. **TNAZ** liquidus temperatures are positioned below its theoretical liquidus curve while those associated with **ADNAZ** are positioned above theoretical in temperature/composition diagrams generated from both initial and remelting operations. As such, neither component is considered to have behaved ideally. Eutectic melting temperatures/compositions (°C/mol percent **TNAZ**) from initial and remelting operations are 75.4/63.8-64.9 and 74.2/61.7-64.0, respectively. The temperatures are averages of the actual measured values, while the compositions are gleaned from the intersections of the "best-fit" trendlines through the respective liquidus temperatures and the average measured eutectic temperatures. The **ADNAZ** and **TNAZ** liquidus trendlines from initial and remelting operations intersect (°C/mol percent **TNAZ**) at 75.8/64.3 and 73.2/62.8, respectively. These trendline intersection temperature values differ from the average measured eutectic melting temperatures by only +0.53 and -1.35 percent, respectively.

Endothermic events, shown to be associated with melting by HSM operation, were observed between eutectic melting and **ADNAZ** liquidus temperatures during initial DSC heating operations (Figure 2). They are described by two near linear trendlines, A and B, that merge and cross the average eutectic melting temperature between 62 and 63 mol percent **TNAZ**. It was demonstrated that solid state heat treatment of a mixture containing 19.7 mol percent **TNAZ**, or simply slow dynamic heating (1 °C/min) without prior heat treatment, causes these melting events to progress from eutectic to B to A to solidus at the expense of the preceding event. The overall data, gleaned from initial heating operations on both heat treated and non-heat treated samples, suggest these events are associated with transition stages that occur during the change from a simple binary eutectic mixture to a solid solution with **TNAZ**. Furthermore, it is believed they are specifically associated with the **ADNAZ** component.

Remelting operations did not appreciably affect the **TNAZ** liquidus temperatures. The **ADNAZ**-rich side of the temperature-composition diagram, however, was converted from that associated with a simple binary eutectic system to one that describes a simple linear solid solution system. The convex-shaped **ADNAZ** solidus curve is continuous (without deflection) to final detectable concentrations of 59.6 (DSC)/69.7 (HSM) mol percent **TNAZ**. The solidus data points were observed as endothermic events by DSC operations and as color changes (accompanied by melting at concentrations less than 52 mol percent **TNAZ**) by HSM operations. Eutectic melting was observed only at **TNAZ** concentrations of 44.5 mol percent and greater. The eutectic melting temperature was shifted from an average value of 75.4 °C during initial melting operations to 74.2 °C. This temperature shift is attributed to the change from a simple **ADNAZ/TNAZ** eutectic to a eutectic between the **ADNAZ-TNAZ** solid solution and **TNAZ**.

CONCLUSIONS

A temperature/composition diagram for the **TNAZ/ADNAZ** binary system has been predicted computationally by using measured heats of fusion and melting points obtained from the neat components. Experimentally, temperature/composition diagrams have been determined for both physical and fused mixtures. Physical mixtures exhibit the thermal characteristics associated with a simple binary eutectic system. Also observed are endothermic transition events that are believed to be associated with the **ADNAZ** molecule and ultimately lead to the solidus line. Fused mixtures exhibit the characteristics associated with a simple linear solid solution system on the **ADNAZ**-rich side of the eutectic and a simple binary eutectic system on the **TNAZ**-rich side. The eutectic melting temperatures (°C)/compositions (mol percent TNAZ) from the physical and fused mixtures are 75.4 /63.8-64.9 and 74.2/61.7-64.0, respectively. Neither component behaves ideally in that their melting temperatures are not positioned on the calculated liquidus curves in either physical or fused mixtures. No evidence suggestive of polymorphism was apparent in the mixtures. An **ADNAZ** polymorphic modification (mp 79.1 °C) was observed during DSC melting operations on neat

ADNAZ (mp 113.7 °C). This binary system was not subjected to small-scale safety testing or scale-up operations due to insufficient quantity of **ADNAZ**.

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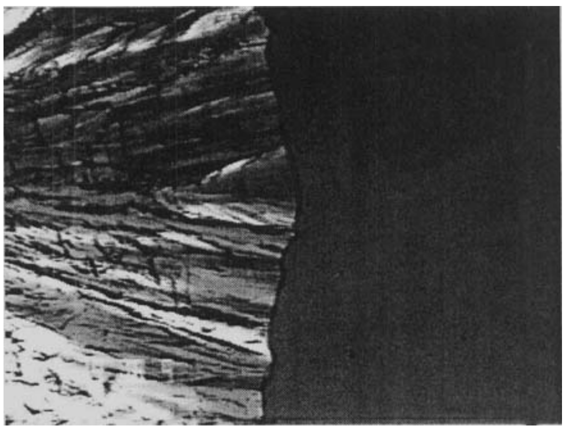


FIGURE 1.

Thin film of **ADNAZ** crystallizing at 37 °C with a formless front and accompanying shrinkage cracks.

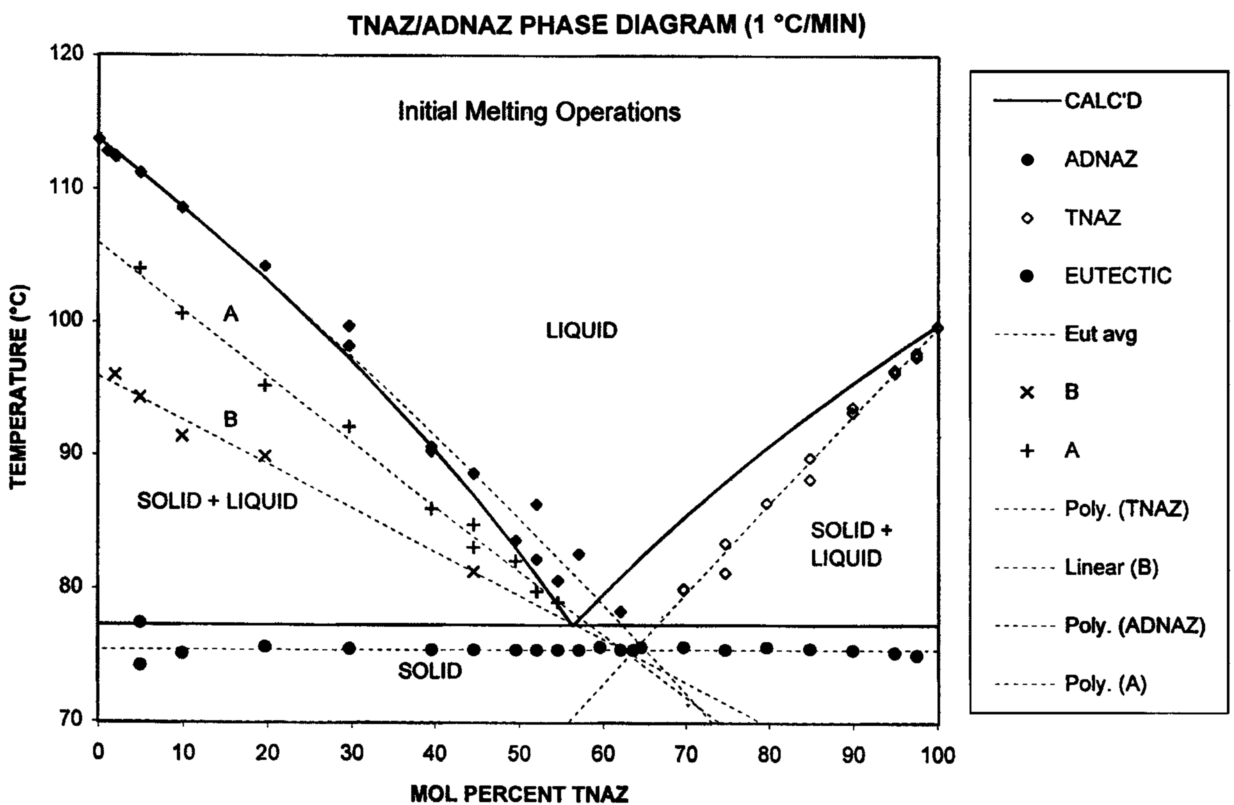


FIGURE 2.

Calculated temperature-composition diagram for the **TNAZ/ADNAZ** system with experimental data from initial melting operations.

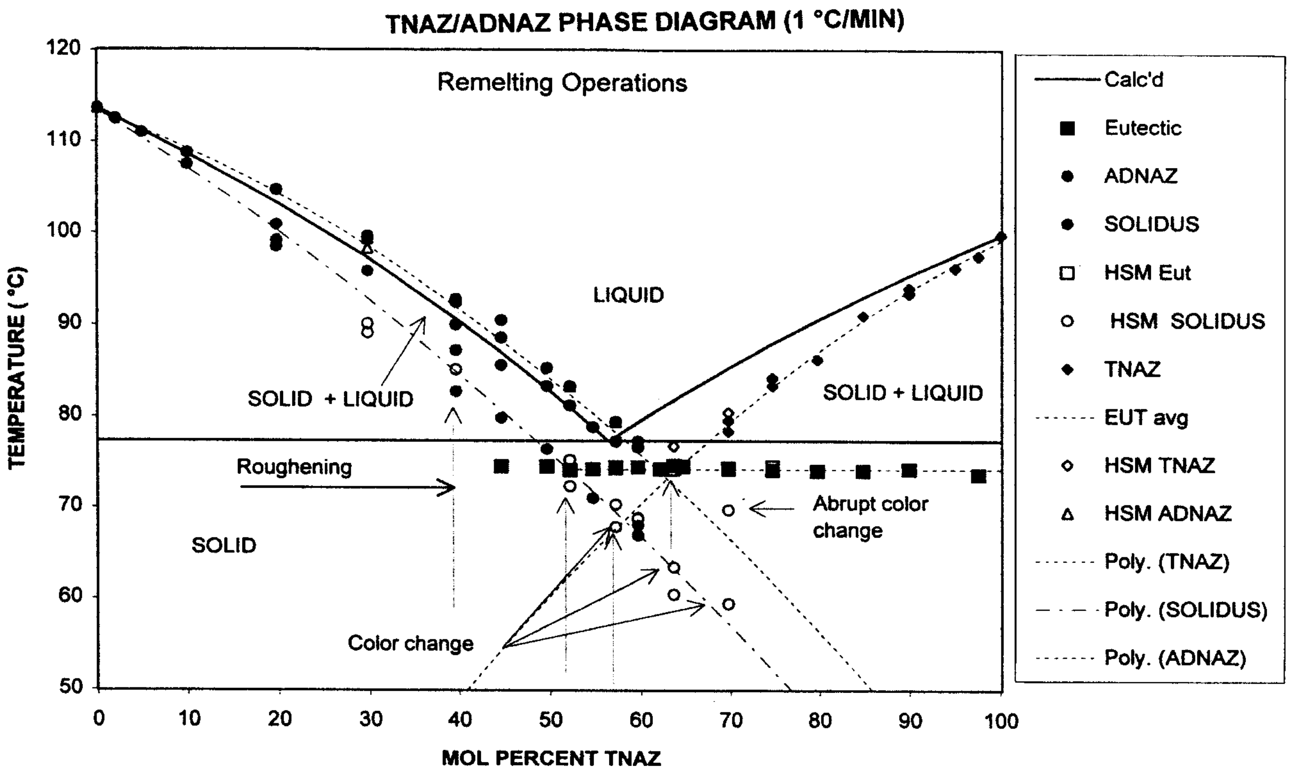
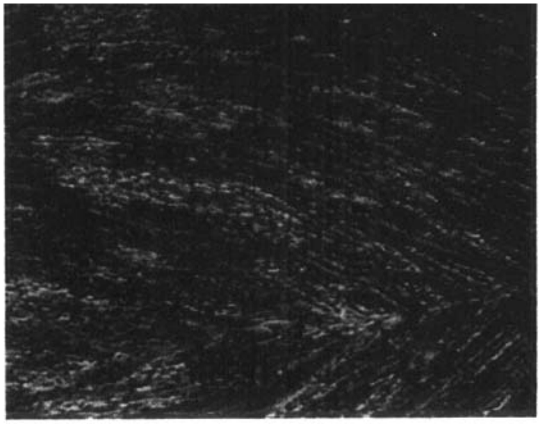
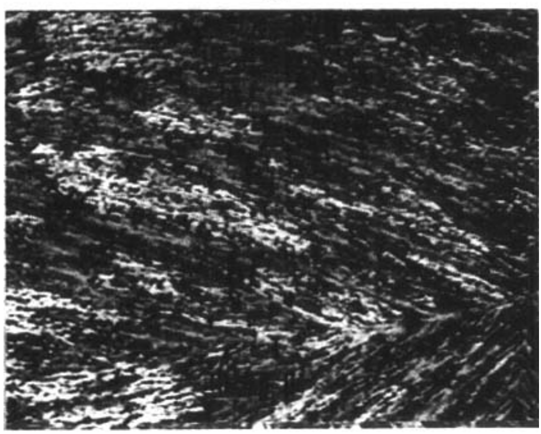


FIGURE 3.

Calculated temperature-composition diagram for the **TNAZ/ADNAZ** system with supporting experimental data from remelting operations.



a.



b.

FIGURE 4.

Color change associated with the solidus temperature for the mixture containing 57.1 mol percent **TNAZ**. (a) 63 °C, (b) 68 °C.

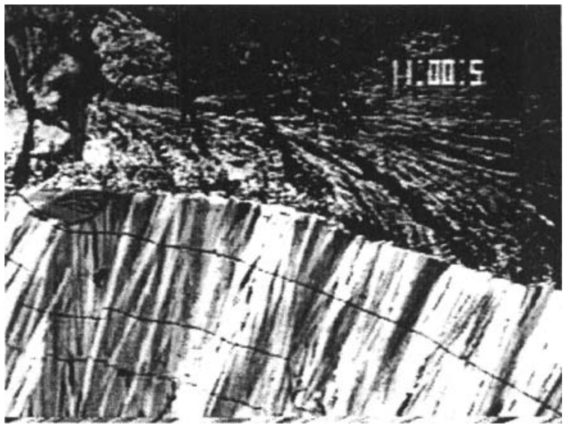


FIGURE 5.

Mixed fusion type thin crystalline film of **TNAZ** (top) and **ADNAZ** (bottom).

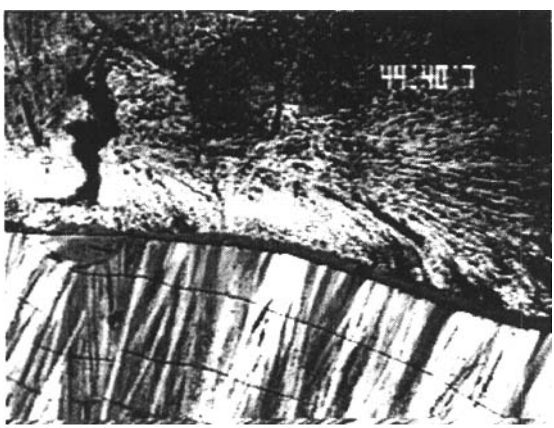


FIGURE 6.

TNAZ/ADNAZ mixed fusion type thin crystalline film showing eutectic melting in the temperature range 72.6-73.9 °C.

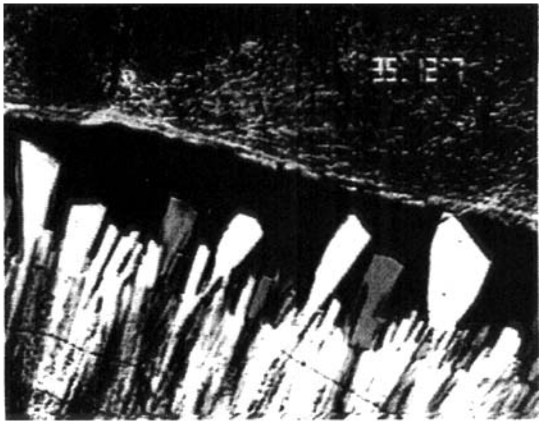


FIGURE 7.

Mixed fusion type thin crystalline film showing **ADNAZ** recrystallizing across the liquid channel between solid **TNAZ** (top) and **ADNAZ** (bottom).

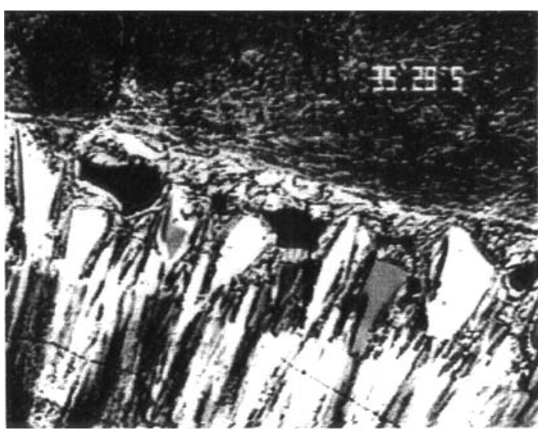


FIGURE 8.

Mixed fusion type thin crystalline film showing final recrystallization product.