ATK THIOKOL PROPULSION

ARDEC Explosives Development: Melt/Pour Explosives Containing TNAZ

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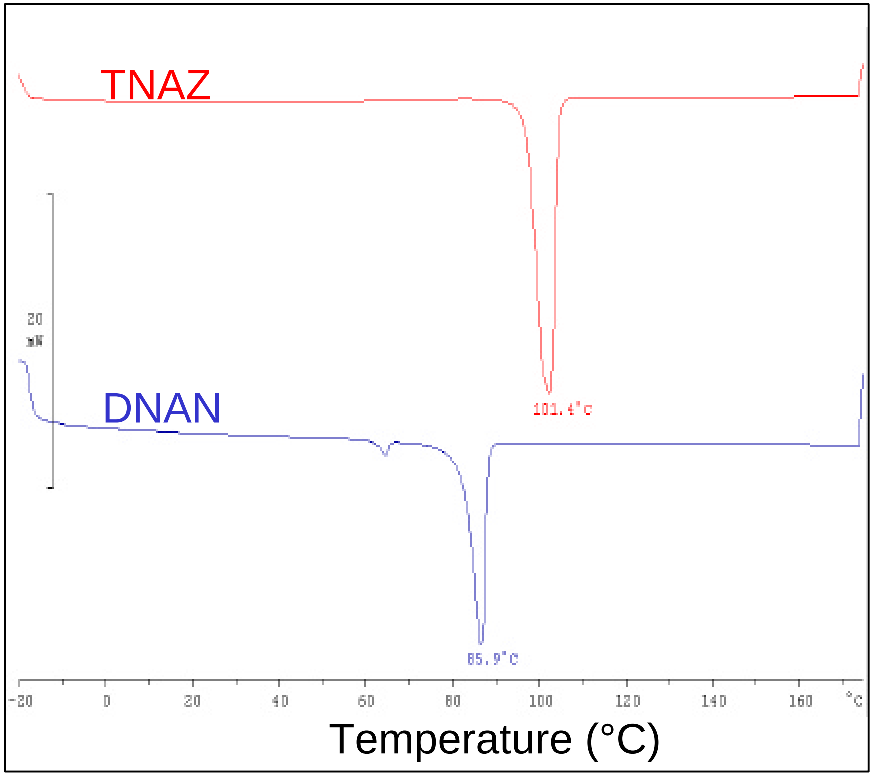
Introduction

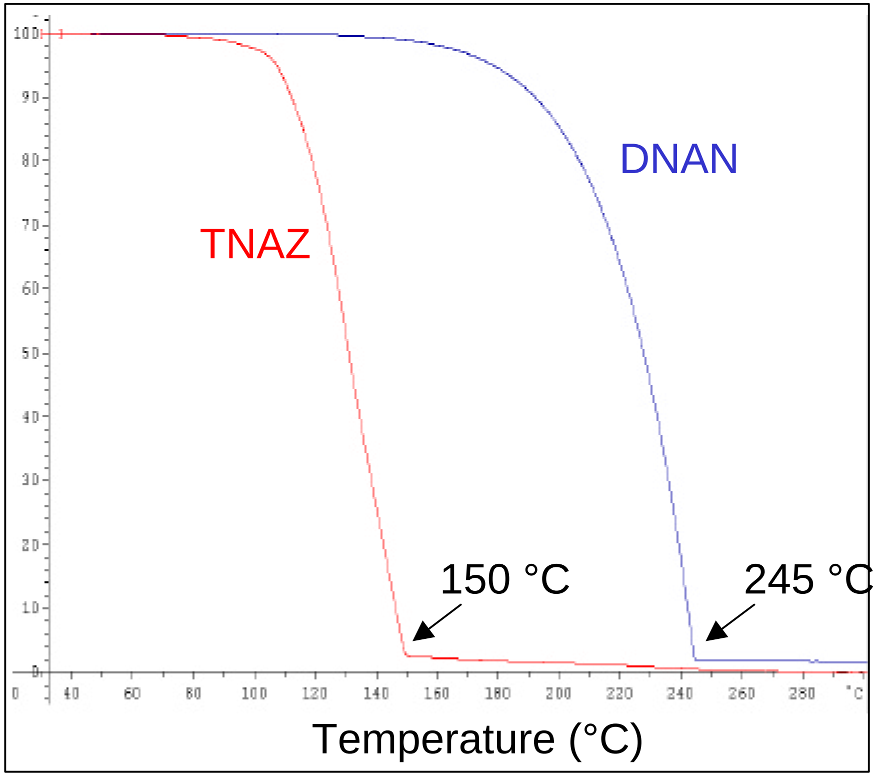
- Objective: To develop a Melt/pour explosive that has the performance of pressed explosives such as LX-14 or LX-19.
  - Why: Melt/pour formulations have advantages in processing and casting simplicity and flexibility and can be exploited in existing production facilities.
  - Why use TNAZ: Performance and melt point (101 °C)

	TNAZ	NQ	RDX	HMX	TNT	CL-20
C-J Pressure (GPa)	35.68	26.40	33.92	38.39	19.09	46.65
C-J Energy (kJ/cc)	4.38	2.92	4.09	4.59	2.38	5.44
C-J Temperature (K)	4659	2818	4220	4127	3712	4592
C-J Shock Vel (mm/μs)	8.95	8.25	8.87	9.23	6.83	9.95
Cylinder Exp (6.5x, kJ/cc)	9.35	5.95	8.71	9.38	5.46	10.96
Etotal of Det. (kJ/cc)	11.06	6.71	10.30	10.98	7.61	12.397

What is the Main Problem with TNAZ?

- DSC and TGA Plots for TNAZ and DNAN





- TNAZ has a higher melting point than DNAN but is more volatile.
- TNAZ volatility is addressed.

What is the Solution?

- Solution: Use commercially available compounds to identify and characterize an optimum TNAZ-eutectic system.
- A eutectic can reduce volatility 3 ways:
  - Lowering the process temperature: 74 °C < process T < 101 °C will lower the volatility.
    - Mixing TNAZ with an organic additive will lower the melt temperature
  - Reducing the mole fraction of TNAZ will reduce the volatility.
  - A Mixture exhibiting non-ideal behavior may have reduced volatility.

How are Eutectics Formed and Characterized?

- Two covalent organics will form a eutectic.
- The composition is related to the difference in the melting points of the compounds.
- The eutectic will be rich (mole fraction) in the lower melting ingredient.
- As the melting points approach equality, the eutectic approaches 50:50 mole ratio of ingredients.
- The mole ratio can be predicted from the melting points:
  - $\ln(X_A/X_B)=-\Delta H_{fus\text{-}eau}/R(1/T_B-1/T_A)$
- The eutectic temperature can then be predicted using the predicted composition.
  - $\ln(X_A)=-\Delta H_{fus\text{-}A}/R(1/T_{eau}-1/T_A)$

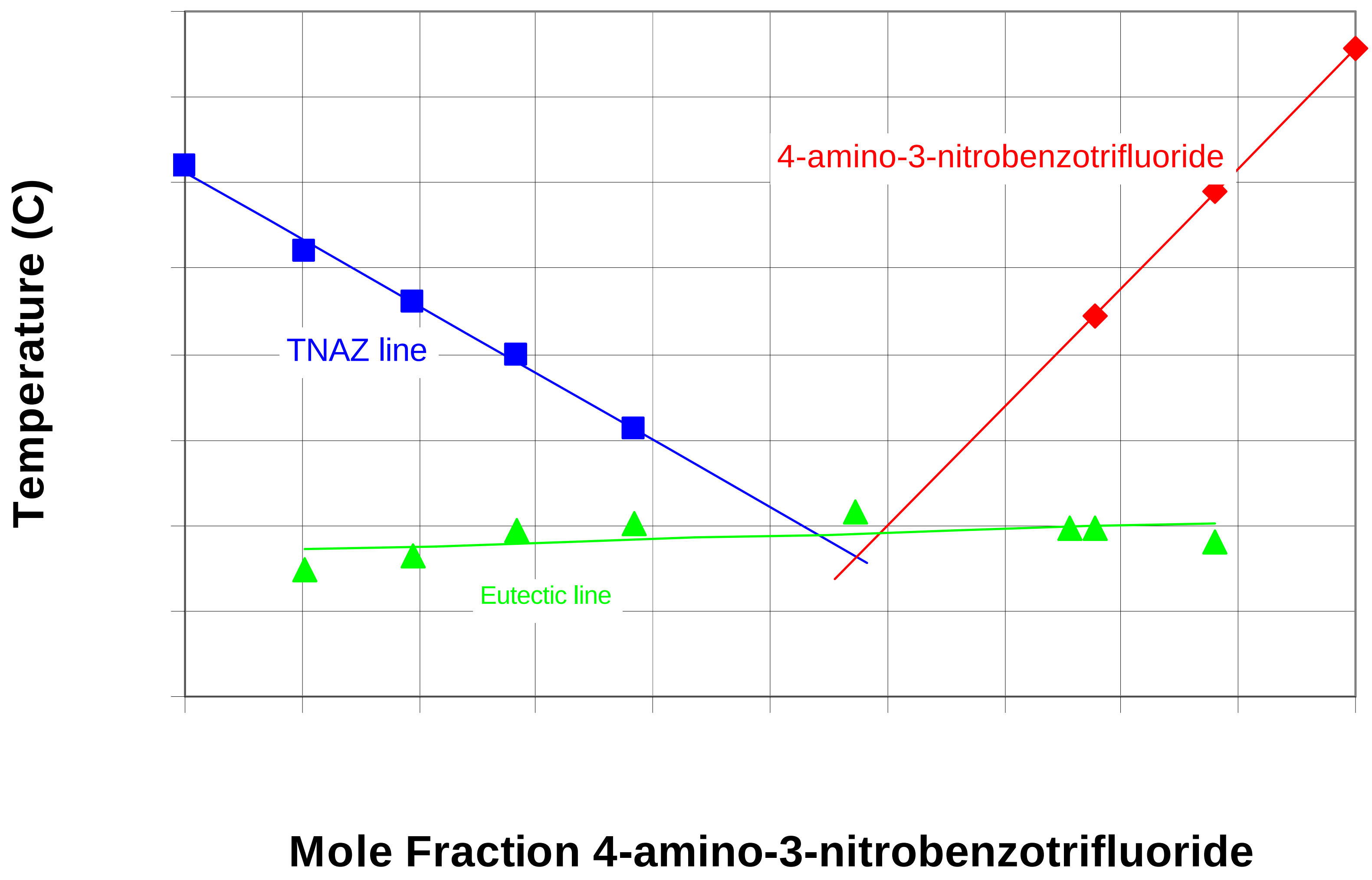
What is Non-ideal Behavior?

- Raoult's Law: $p_A = x_A p_A^*$
- $p_S = p_A + p_B$
- Non-ideal behavior is when the vapor pressure of the system is more or less than that predicted by Raoult's Law.
- Dissimilar species deviate strongly from Raoult's law.
  - Even they conform when nearly pure (>95% one component)
- If molecular interactions are unfavorable the mixture is destabilized and the vapor pressure is increased relative to ideal.
- If the interactions are favorable then mixture is stabilized and the vapor pressure is reduced relative to ideal.
- If the components are very similar the mixture acts ideal.

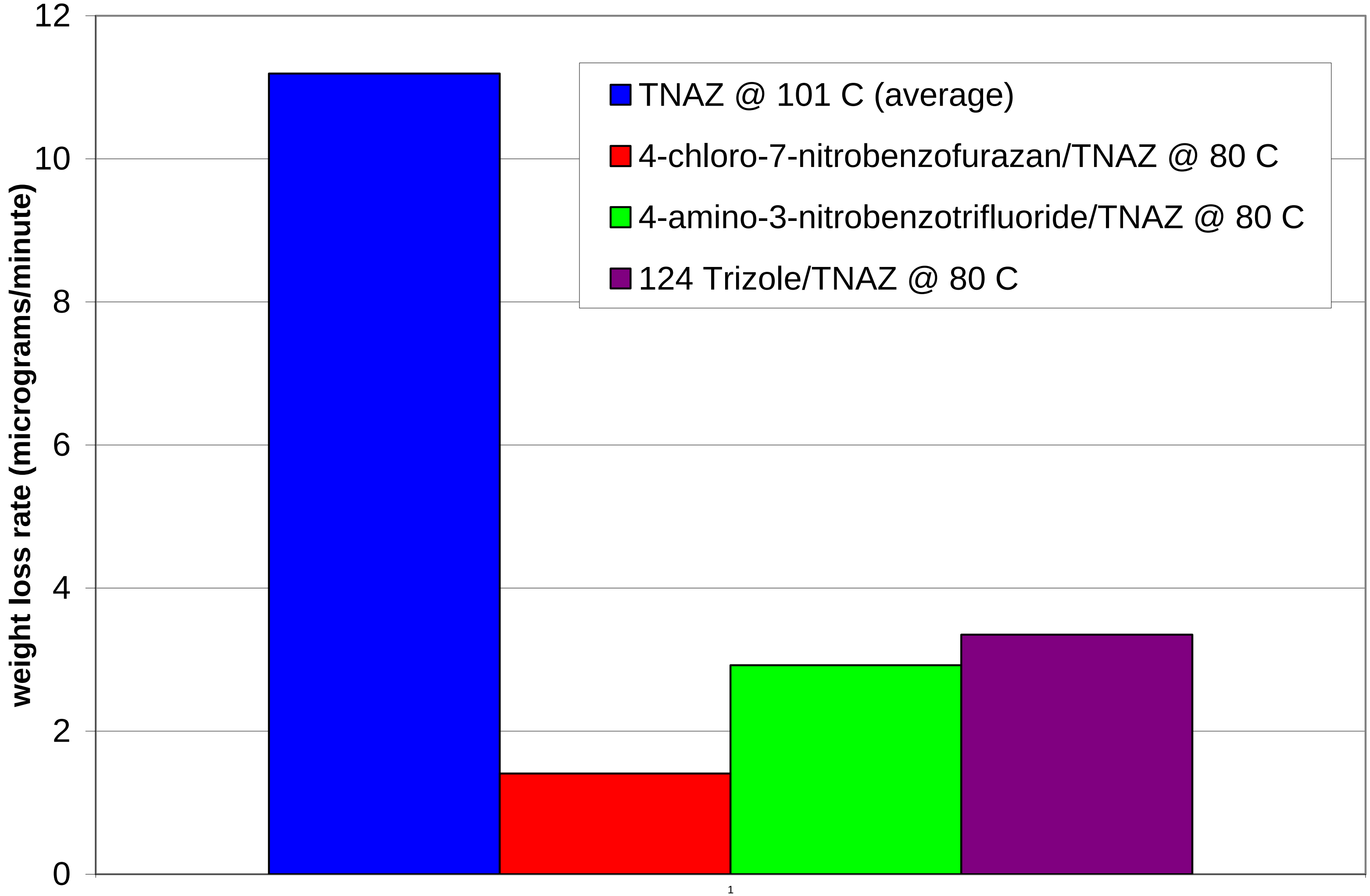
Additive Identification

	Material	Material Molecular Weight	Material MP (DSC, 3rd cycle, °C)[1]	MP diff from TNAZ (°C)	Theoretical %TNAZ in Eutectic by weight	Predicted Eutectic MP °C
	TNAZ	192.09	101.0	0	NA	NA
	Melt additives					
1	Aminoguanidine nitrate	137.11	146.8	45.8	83.6	90.5
2	1,4-Diphenylbutadiyne	202.26	87.2	13.8	39.6	65.0
3	3,5-Dinitro-4-methylbenzoic acid	226.14	159.0	58.0	80.9	93.0
4	1-Methyl-3-nitroguanidine	118.1	160.4	59.4	89.3	93.3
5	2,4-Dinitroanisole	198.14	85.9	15.1	39.0	64.0
6	4-Chloro-7-nitrobenzofurazan	199.55	98.3	2.7	48.6	72.2
7	Benzotriazole	119.13	96.7	4.3	60.1	71.2
8	3,5-Dinitrobenzyl alcohol	198.13	89.6	11.4	42.0	66.6
9	Methyl 4-nitrobenzoate	181.15	95.9	5.1	49.2	70.8
10	4-Amino-3-nitrobenzotrifluoride	206.12	107.8	6.8	55.0	77.4
11	5-Nitro-2-furaldehyde DA	243.18	87.3[2]	13.7	35.3	65.0
12	1,2,4-Triazole	69.07	121.2	20.2	84.3	83.3
13	2-Oxazolidone	87.08	89.1	11.9	61.8	66.3

Liquid Phase Diagram

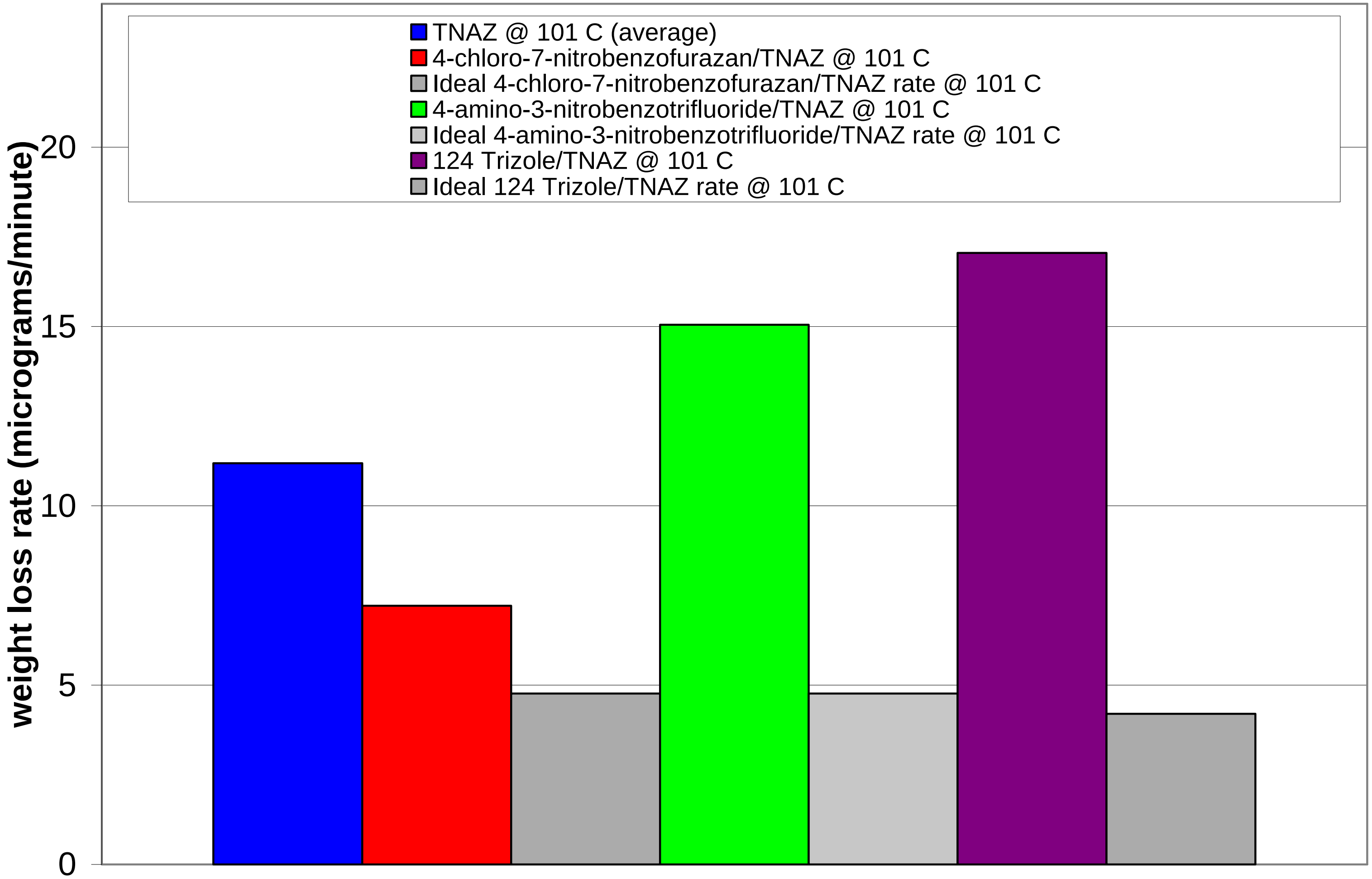


What is the Volatility Reduction vs. Pure TNAZ?



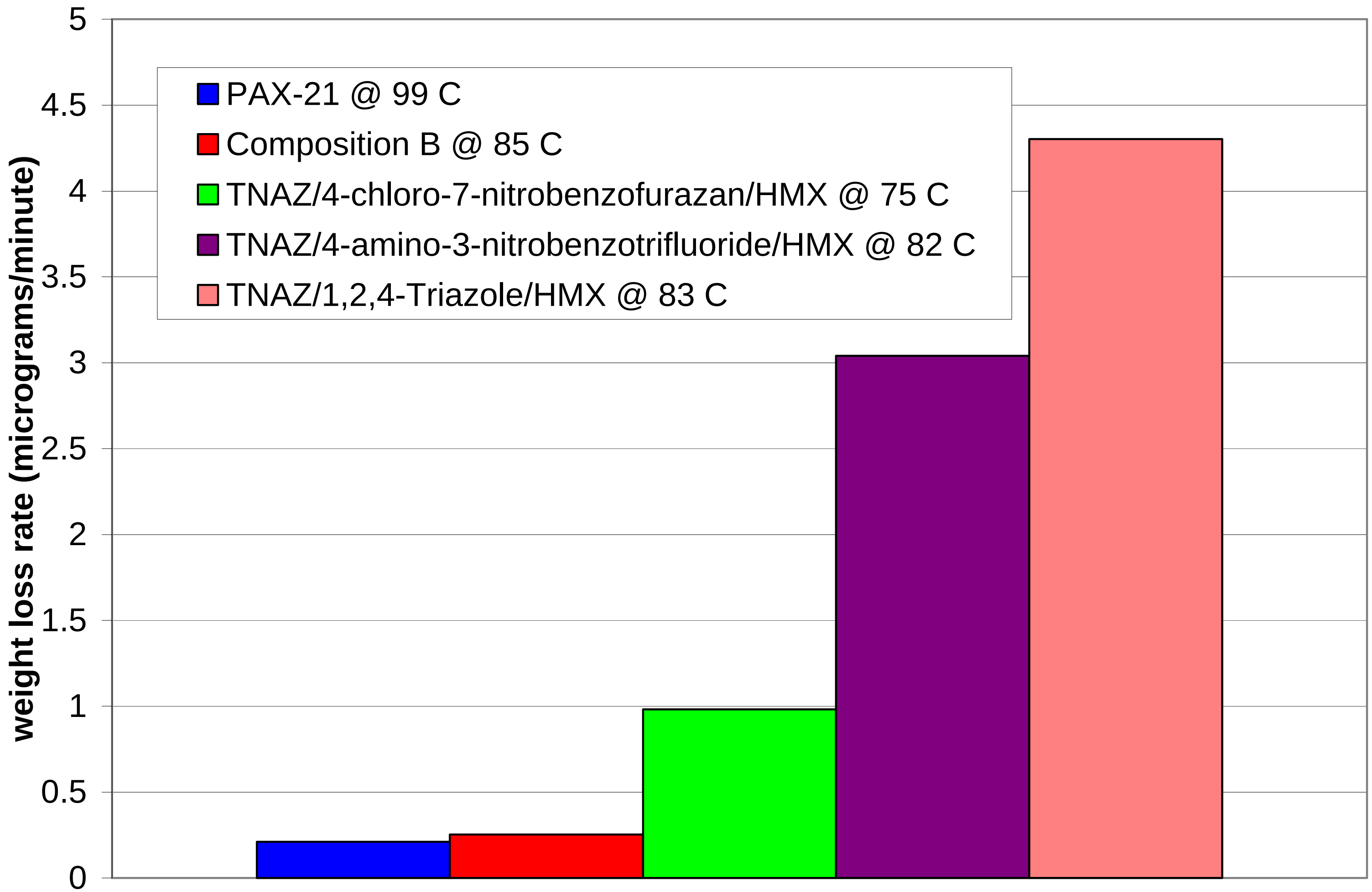
- Volatility of these Melt/pour binders is loser than pure TNAZ (both melt phase).

Is Non-ideal Behavior Observed?



- Non-ideal behavior is seen in the wrong direction.

How Does the Volatility Compare to Melt/pour?



- Volatility still higher than current Melt/pour formulations.

Processing Study

- Explosives made using a 40/60 by weight TNAZ/4-amino-3-nitrobenzotrifluoride eutectic as binder.
- Formulations examined for pourability at 85 °C.
- Fillers are RDX, HMX, and CL-20.

	RDX	HMX	CL-20
Solids level all fine	47	58	44
Coarse to fine ratio 70% solids	56/44	50/50	60/40

- Processability using TNAZ/additive eutectics is comparable to PAX-21.

Thermochemical Data

Additive number	Material	CAS#	Formula	ΔHf (kJ/mol)	Density (g/mL)
	estane	-	$C_{10}H_{14.6}N_{0.37}O_{3.42}$	-773	1.18
	HMX	-	$C_4H_8N_8O_8$	74.75	1.905
	TNAZ	-	$C_3H_4N_4O_6$	0	1.832
Additives					
2	1,4-Diphenylbutadiyne	886-66-8	$C_{16}H_{10}$	536[1]	1.124[3]
4	1-Methyl-3-nitroguanidine	4245-76-5	$C_2H_6N_4O_2$	-67.4[1]	1.489[3]
6	4-Chloro-7-nitrobenzofurazan	10199-89-0	$C_6H_2N_3O_3Cl$	264[4]	1.663[3]
7	Benzotriazole	95-14-7	$C_6H_5N_3$	243[2]	1.423[3]
10	4-Amino-3-nitrobenzotrifluoride	400-98-6	$C_7H_5F_3N_2O_2$	-810[4]	1.601[3]
12	1,2,4-Triazole	288-88-0	$C_2H_3N_3$	109.7[2]	1.466[3]

[1] from heat of combustion data found at www.webbook.nist.gov
[2] data from www.webbook.nist.gov
[3] calculated by functional group additivity.
[4] from measured heat of formation data.

Explosive Formulation Performance

Ingredient	Weight%			
LX-14 (95.5% HMX)	100	-	-	-
CL-20	-	70	70	70
TNAZ/1,2,4-Triazole (**12**)	-	30	-	-
TNAZ/4-Amino-3-nitrobenzotrifluoride (**10**)	-	-	30	-
TNT	-	-	-	30
Performance				
C-J Pressure (GPa)	34.43	38.74	38.60	36.23
C-J Temperature (K)	3981	4343	3738	4383
C-J Shock Vel (mm/μs)	8.80	9.16	8.63	8.79
Cylinder Exp (6.5x, kJ/cc)	8.59	9.39	8.62	8.96
Etotal of Det. (kJ/cc)	10.27	10.97	10.09	10.67

- Observed detonation velocity 8.68 mm/μs.

Conclusions

- Eutectics with TNAZ were prepared and characterized.
  - Compositions and melting points were predicted and measured.
- Melt/pour binders containing TNAZ with 3.3-8.0 fold reductions in volatility vs. pure TNAZ were identified and characterized.
- Non-ideal behavior was observed but it was in the wrong direction.
- Melt/pour explosives based on the eutectics still have 5-21 times the volatility of PAX-21 at process temperatures.
- Melt/pour explosives can be processed with at least 70% CL-20 using a ratio of coarse to fine material.
- A melt/pour explosive with a detonation velocity of 8.68 mm/µs was demonstrated.
  - +6.9% detonation pressure, +4.2% detonation velocity over TNT-based
- More additives need to be screened now that the tools are firmly in hand.
  - Additives with better Heats of formation and density.
  - Eutectics with higher TNAZ content.
  - Lower volatility, non-ideal behavior not yet optimized.