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Malcolm Baldrige National Quality Award 2007 Award Recipient

Scale –Up of the Insensitive Energetic Binder, Cellulose Acetate Nitrate (CAN)

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

Outline

- Acknowledgement
- Technology, Objectives and Goals
- Background
- CAN Binder
- CAN Binder with Ground FOX-12
- Characterization
- Recommendations & Conclusions

Acknowledgements

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  - **Jeffrey Wyckoff**
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  - **Dr. Chris Michienzi**
- **ATK, Radford AAP**
  - **Jim Wedwick**
  - **Christopher McMurray**
  - **Dr Steven Ritchie**
- **Army Aviation and Missile Command, Redstone Arsenal**
  - **Dr. Jamie Neidert**

Technology, Objectives & Goals

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❖ Technology

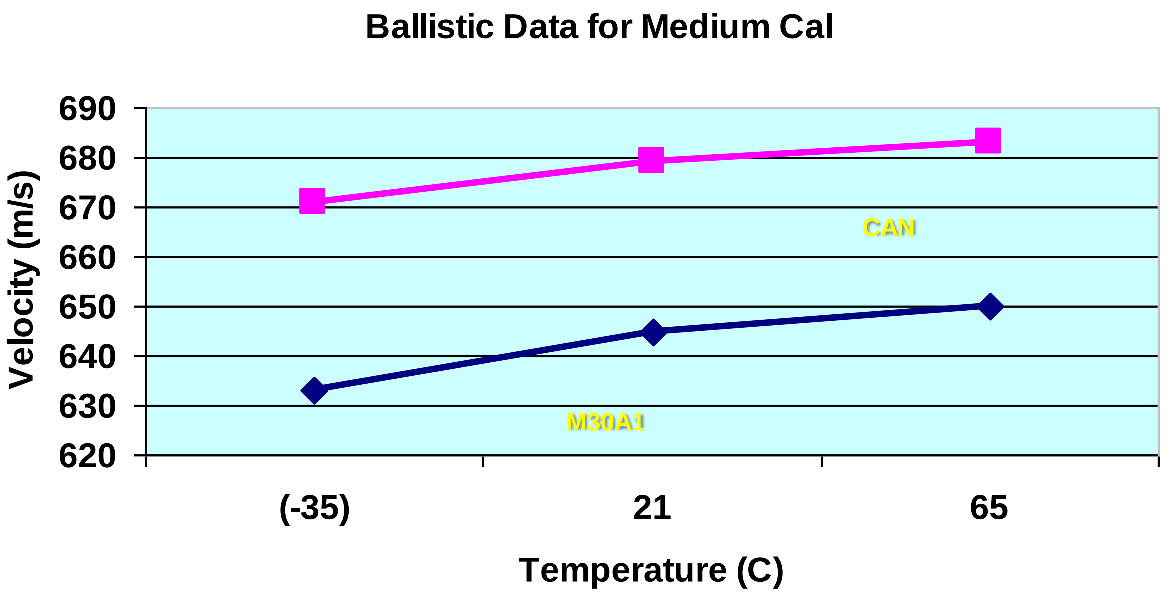
- A new family of high energy insensitive propellants with Cellulose Acetate Nitrate (CAN) based binder and ground FOX-12 energetic filler.

❖ Objectives

- Improved ballistics across temperature range
- Critical diameter less than 2X ballistic diameter
- 5 lbs pendulum displacement less than 10 cm with RHA 100mm
- Ignition temperature > 550°C in hot fragment conductive ignition
- Acceptable mechanical properties
- Demonstrate large caliber propellants with improved Insensitive Munitions properties (IM):
  - Slow and Fast Cook-Off, Bullet Impact, Fragment impact and Shaped Charge Jet explosion reaction

Background

- ARDEC and Japan Defense Agency evaluated a series of propellant formulations with CAN binders through a cooperative research



CAN based formulation delivered ~5% performance gain

Initial IM testing was Encouraging

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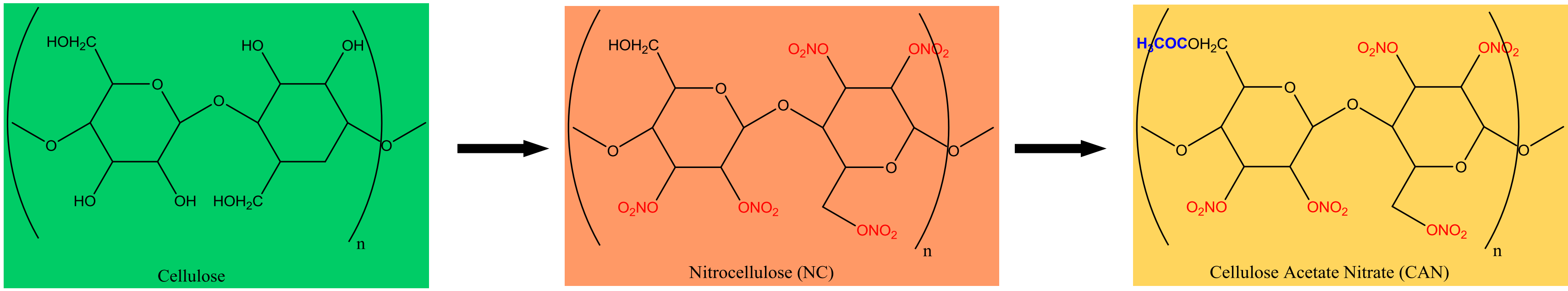
Test	Passing Criteria	M30A1	CAN Propellant
FCO	Burn V	Pass V	Pass V
SCO	Burn V	Not Tested	Not Tested
BI	Burn V	Fail III-IV / IV	Better >V, IV, >V
FI	Burn V	Fail III / III-IV	Better III-IV, III-IV, IV-V
SCJI	No Detonation V, IV,III	Pass III	Pass III

Improved IM with both BI and FI

Technical Approach

- **The traditional synthesis of CAN has been known for years**

Nitration **Acetylation**



Cellulose + mixed acid **NC (+ acetic anhydride)** **CAN**

- **Challenges with the traditional synthesis**
  - Use of toluene is environmentally unfriendly
  - Several washing steps

AES at RFAAP working to improve traditional route

Synthesis at Radford

- **Scale-up CAN from Radford NC**
  - Pilot plant effort (100 gallon reactor)
  - Characterize process and material
- **Synthesis of CAN from cellulose acetate (CA)**
  - Lab study to test feasibility
  - Potential low cost route to CAN
    - Fiber acetylated CA used to retain fiber structure
    - Eliminate toluene and multiple washing steps

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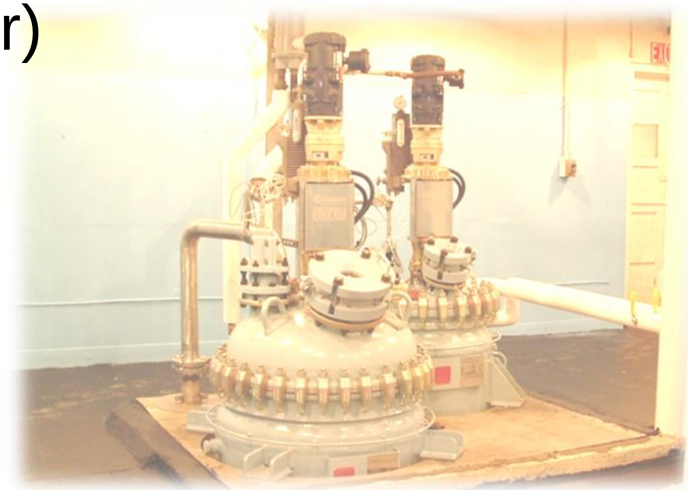
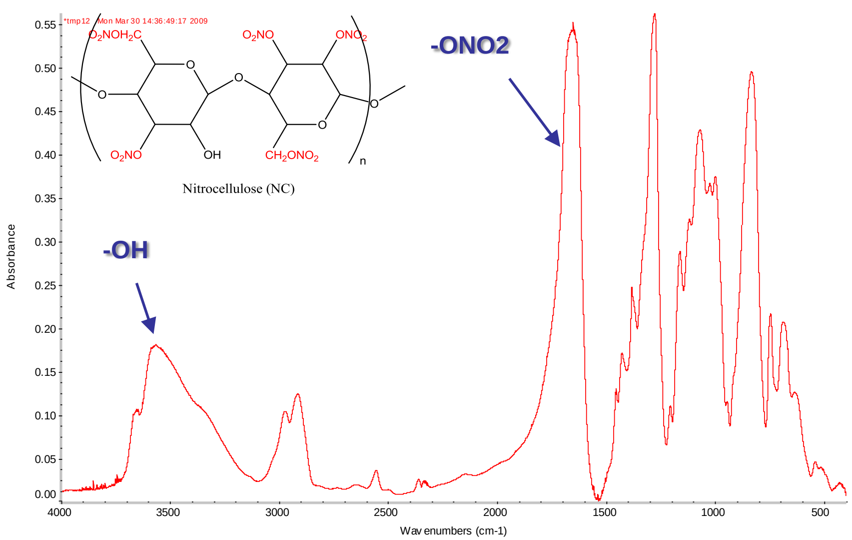
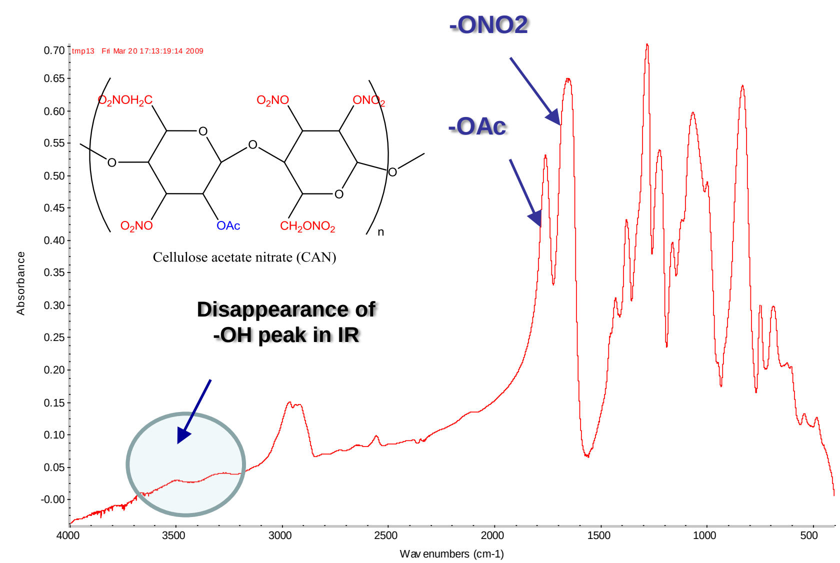


Pilot facility on-line & ideal for CAN scale-up

ATK CAN Synthesis

- ATK investigated the synthesis of CAN using Radford NC
  - Synthesis completed using both *p*-Toluenesulfonic Acid and Perchloric Acid ($HClO_4$) catalysts
  - Perchloric Acid provided higher degree of acetylation
    - Higher degree of acetylation may have been a result of denitration





ATK results provide an excellent starting point for further optimization

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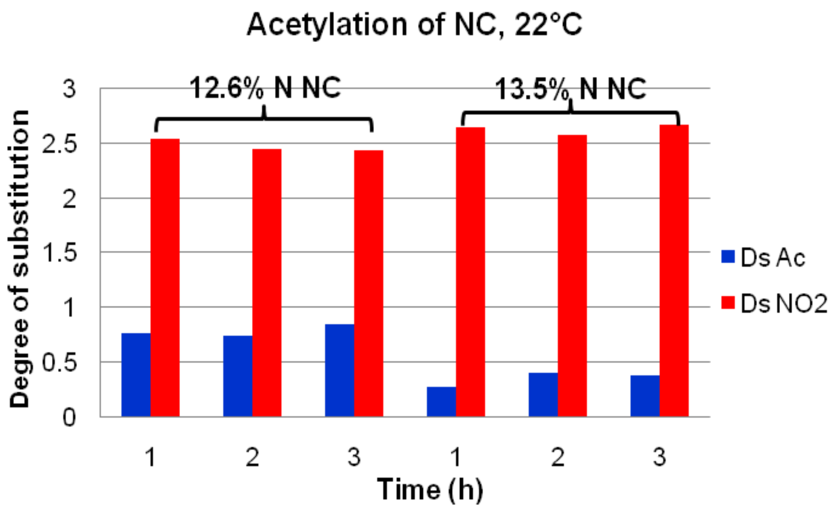
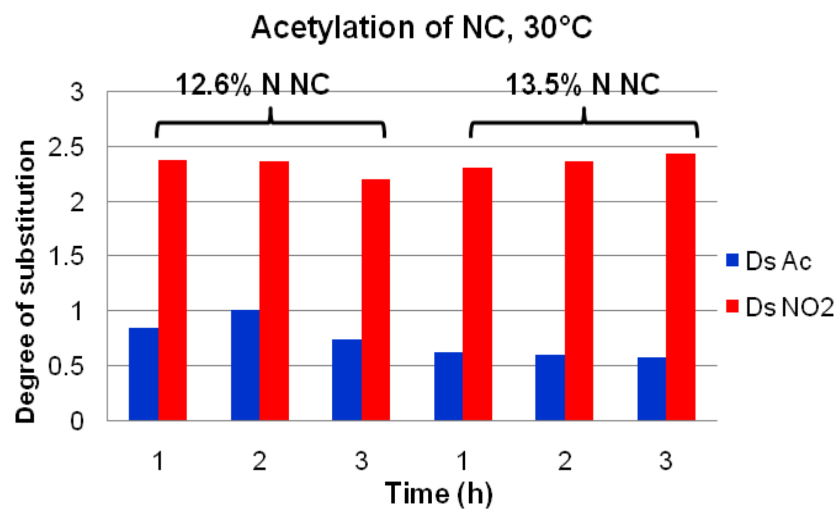
CAN Lab Optimization





- **Lab experiments used to establish conditions for pilot scale runs**
  - **Denitration with extended reaction times & at higher reaction temp.**
    - Desired Ds NO2 2.3-2.8; Ds Ac 0.2-0.7;Ds OH 0.2 or less
    - Recommended Ds NO2 + Ds Ac + Ds OH = 3.0
    - Ds NO2 = 2.2-2.29 =Denitration
    - Ds Acet < 2 get denitration
  - **Ap**pearance of -OAc peak (CAN) in FTIR

Excellent correlation between expected and demonstrated acetylation level

CAN Pilot Scale Results

Test	Requirement	Lab kg lot	Pilot lot 1	Pilot lot 2	Pilot lot 3
%N		11.13	11.96	11.81	11.73
%Ac		7.96	8.23	8.07	8.47
Mw	>100,000	N/A	395,334	372,349	389,180
Practical Fiber Length	80% fiber between 100 µm and 1 mm	N/A	81.34%	80.87%	80.31%
Density (g/cm³)	Versus NC (1.36)	N/A	1.07	1.09	1.15
Heat of Expl. (cal/g)	>11% N NC (734)		733.5	618.1	671.1
Heat of Formation, KJ/mole	NC11(-756) NC12.6 (-708) NC13(-690) NC13.4(-678)	-753	-762		
Solubility (ether/acetone)	99% minimum	N/A	1.93	1.96	1.48
65.5 ºC heat test	> 35 min	45+ min	45+ min	45+ min	45+ min

- Used lab results for scale-up guidance
  - Blended 12.6%N & 13.5%N NC to provide higher Ds NO2 in final product
- 13.2%N NC used as final blend (Ds nitrate 2.80)
  - Over 100 lbs of CAN produced in three runs
- Excellent batch-to-batch product consistency
  - Testing against preliminary requirements (NC based)

Scalable process using Radford NC

Acetylation:

- Any free hydroxyl groups are replaced by acetate
- The number of nitrate ester groups per molecule does not change
- The number of carbons and oxygens and hydrogens per molecule increases
- Therefore the wt% of N per molecule decreases

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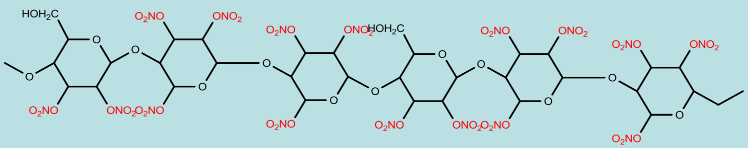
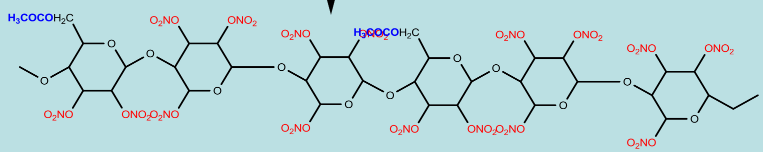


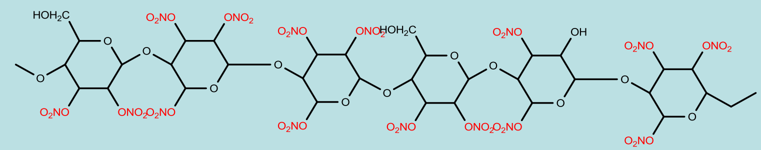
Elemental Analysis: C, 25.01; H, 2.64; N, 13.33; O, 59.02

Acetylate the unsubstituted OHs



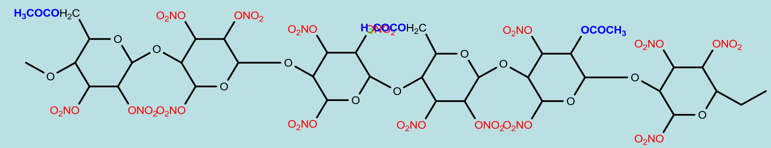
Elemental Analysis: C, 26.54; H, 2.74; N, 12.70; O, 58.02

Expect 13.33%N to finish as 12.70%N
Two acetate group per 6 monomer units



Elemental Analysis: C, 25.70; H, 2.77; N, 12.84; O, 58.68

Acetylate the unsubstituted OHs



Elemental Analysis: C, 27.95; H, 2.92; N, 11.92; O, 57.21

Expect 12.84%N to finish as 11.92%N
Three acetate groups per 6 monomer units

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CA Pathway to CAN

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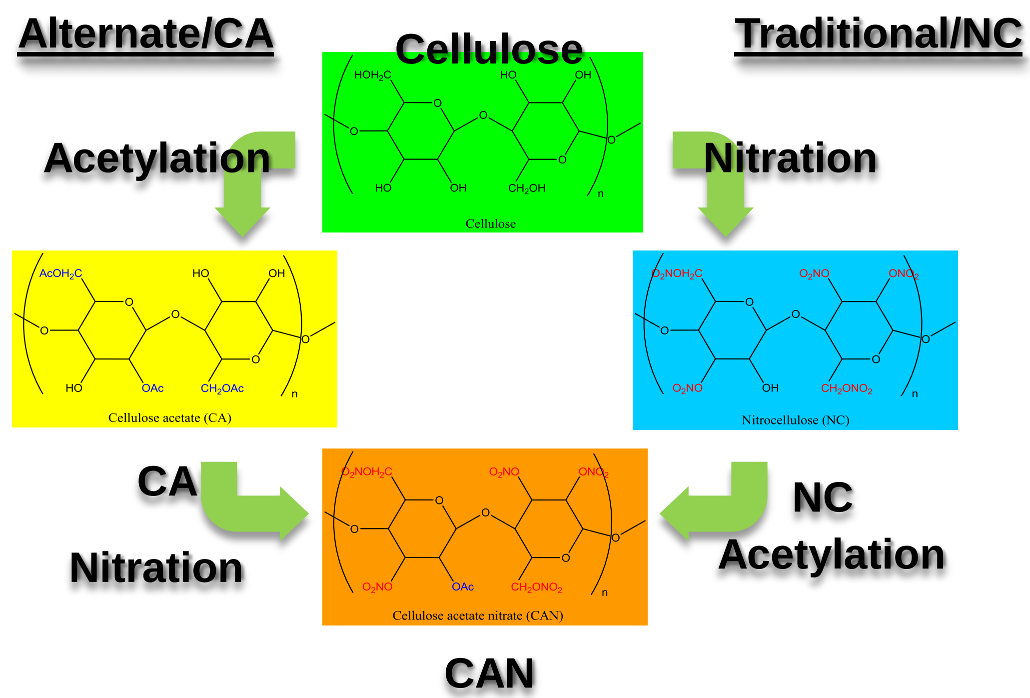
- **Alternate route to CAN**
  - **Start with CA (commodity)**
    - No toluene in process
    - Cellulose acetate from commercial source
    - Manufacturing infrastructure in place for both acetylation and nitration
  - **Early results not encouraging**
    - Use of NC mixed acids leads to high degree of deacetylation & low degree of nitration



Process optimization being explored

Small Scale Sensitivity Data of CAN

THRESHOLD INITIATION LEVEL (TIL)[1]

Propellant		Temp		Impact[2]			Sliding Friction[3]		Electrostatic Discharge[4]	Thermal[5]
				Thick	Ht.		Vertical Force			
Type	State	°F	%TV	(mils)[5]	(cm)	ft-lb	(lb/fps)	(psi)	(joules)	(°C)
Cellulose Acetate Nitrate										
CAN	Dried Crushed	70	dried	11-13	17	2.0	142/8	37,270	0.0648	Flame 217.6
CAN	Ethanol wet	70	69	10	≥120	≥14.4	705/8	106,624	--	--
Cellulose Butyrate Nitrate										
CBN	Ethanol wet	70	38.3	26	100	12.2	960/8	129,730	--	
CBN	dried	70	dried	9-10	64	7.7	395/8	74,178	0.0785	Flame 229.8

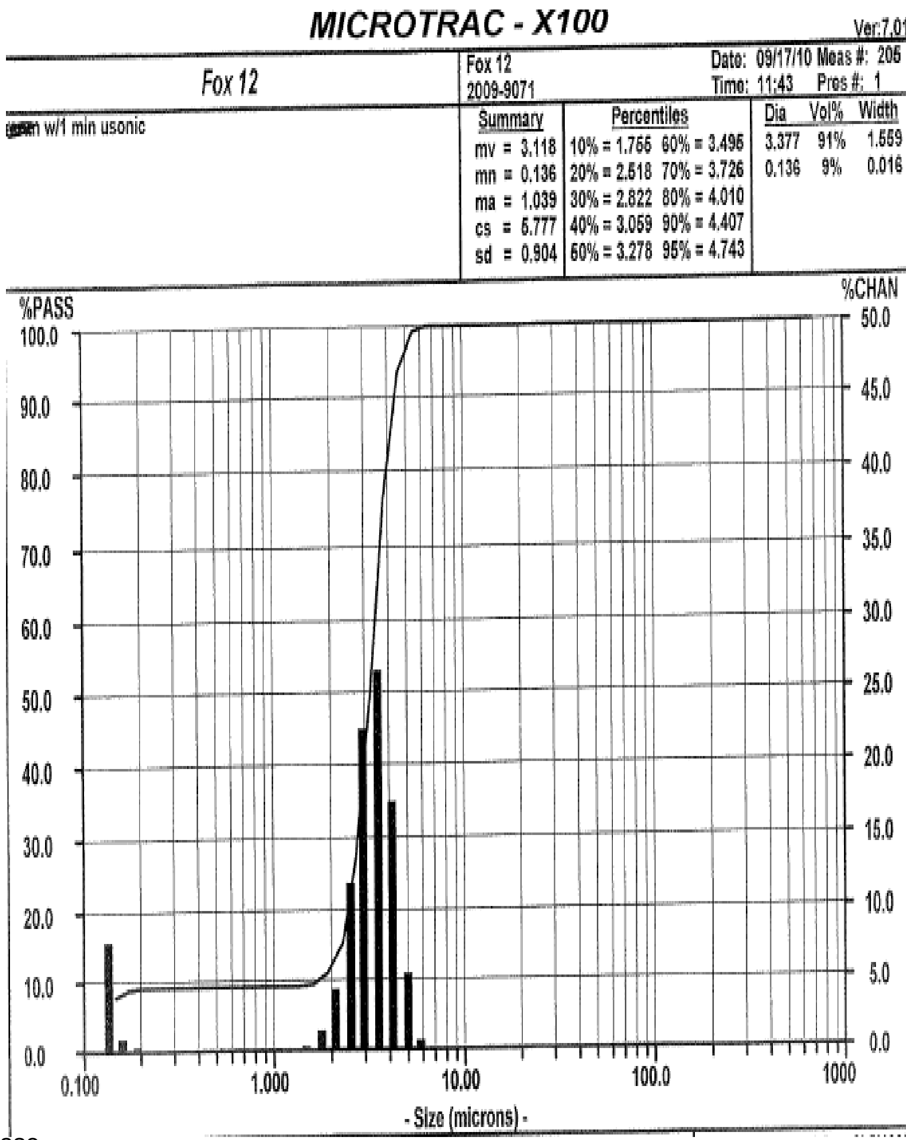
1. TIL - Defined as the level above which initiation can occur, as established with twenty consecutive failures obtained at the indicated level and initiation detected at the next higher level. Testing was performed using MGR tool steel test components having 50-70 micro-inch surface finish and a hardness range of 58-62 (Rockwell C). Sample initiation detected by infrared analysis of decomposition gases (CO, CO_2, N_2O, NO).
2. Modified Bureau of Mines test machine - 2 Kilogram falling weight.
3. ABL Sliding Friction Machine.
4. Electrostatic Discharge Test - Modified Bureau of Mines test in which selective capacitors are charged at a constant 5,000 volts and discharged through a variable air gap.
5. Unless otherwise stated, thermal data is derived from the "Fisher johns" melt point analyzer test where a small sample specimen is placed on an anvil and heated slowly until it decomposes.

ARDEC CAN BASED PROPELLANT FORMULATIONS

Table 2: Thermochemical Properties of Proposed Preliminary Propellant Formulations

	M31A2	w/ NQ	w/ FOX-12
NC12.6	X		
CAN11.73		X	X
RDX			
FOX-12			X
Solid Filler	X	X	
BDNPA/F			
Plasticizer A			
Plasticizer B			
Plasticizer C	X	X	X
Akardit II			
Ethyl Centralite	X	X	X
Plasticizer F	X	X	X
Flash Suppressant	X	x	X
Cryolite			
TOTAL	100.00	100.00	100.00
Density (g/cc)	1.6697 00	1.5214	1.5153
Flame Temp (K)	2646.0	2954	3133
Impetus (J/g)	988.99	1083.35	1079.74
Covolume (cc/g)	0.941	0.917	0.903
C_P/C_V (γ)	1.266	1.252	1.235
Energy Density [$I\rho$]	1651	1648	1636
% Reduction in $I\rho$	-	0.19%	0.92%
NC/CAN:Plasticizer	1.0238	1.0238	1.0238
Solids:Liquids	3.7619	3.7619	3.7619

All CAN received from ATK, Radford AAP were 56.05% alcohol wet.



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ARDEC CAN BASED PROPELLANT FORMULATIONS THERMOCHEMICAL PROPERTIES

	M31A2	PAP 10-029	PAP 11-057	PAP 11-064	PAP 11-065
NC12.6	X				
CAN11.73		X	X	X	X
Solid Filler A		X			X
FOX-12		X			X
Solid Filler B	X				
Plasticizer A		X		X	
Plasticizer B		X		X	
Plasticizer C			X		
Plasticizer D					X
NG	X				
Stabilizer II		X	X	X	X
Ethyl Centralite	X				
Dibutylpthalate	X				
Flash Suppressant	X				
TOTAL	100.00	100.00	100.00	100.00	100.00
Density (g/cc)	1.665054	1.635648	1.612813	1.584865	1.591271
Flame Temp (K)	2639.2	3022.3	3116.8	2804	2898.4
Impetus (J/g)	984.49	1105.90	1021.65	970.39	1033.29
Covolume (cc/g)	1.028	1.015	0.943	0.971	0.984
C_P/C_V (γ)	1.263	1.253	1.235	1.249	1.248
Energy Density [$I\rho$]	1639	1809	1648	1538	1644

CAN, Plasticizer B , (Acetone/Ethyl Alcohol)

PAP-10-057

BR= AP^B

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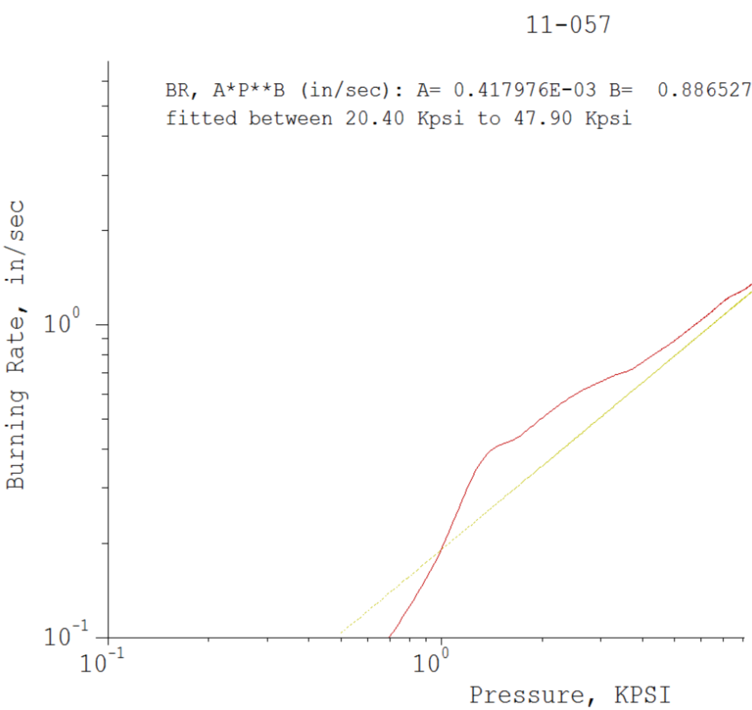
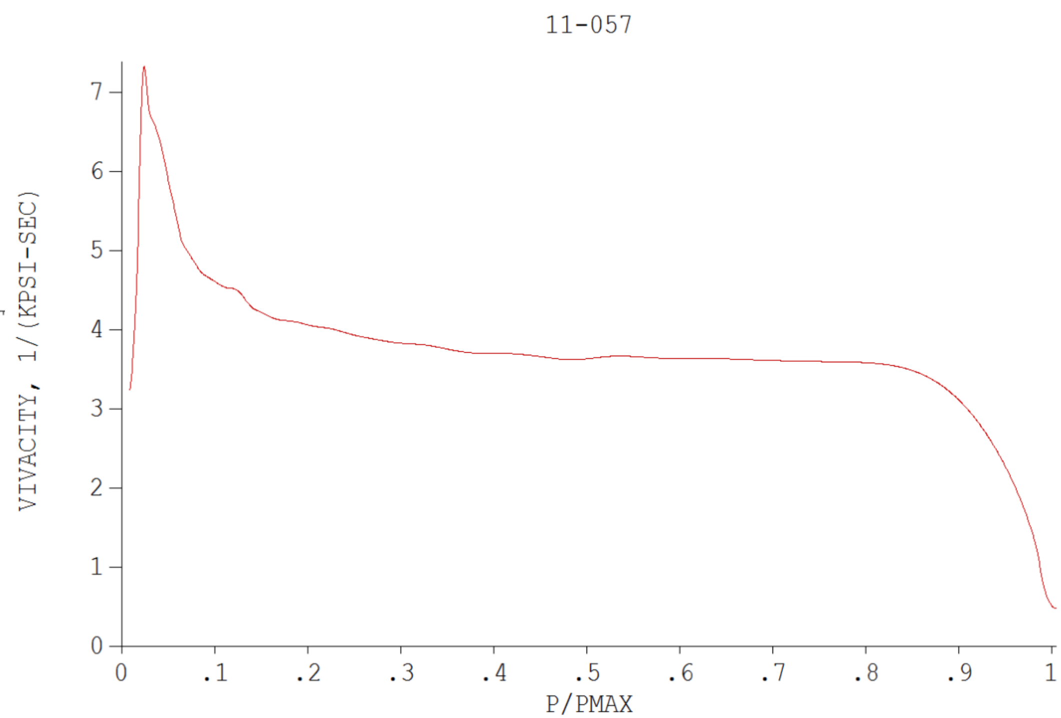




PAP-10-064 (ARDEC)

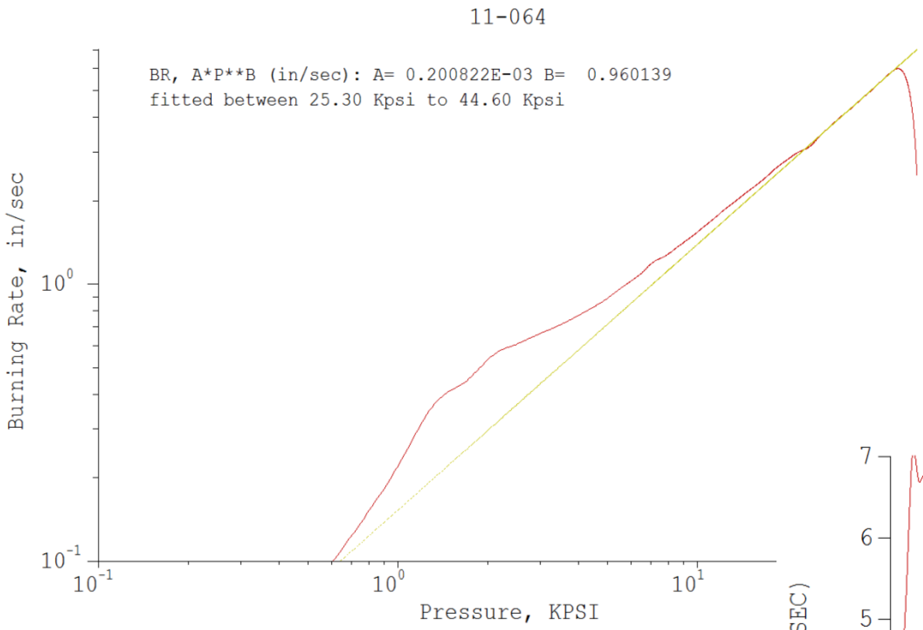
Mixing (Horizontal Sigma Blade)

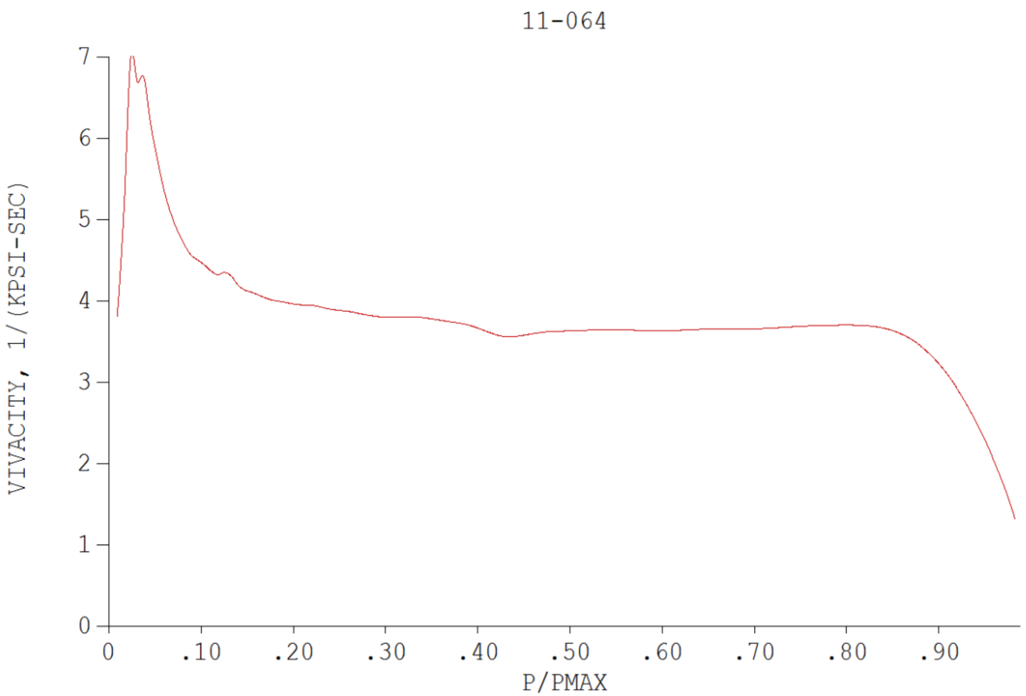
Extrusion (Ram Press)

CAN,
PLASTICIZER A, 1PLASTICIZER B, (Acetone/Ethyl Alcohol

PAP-10-064 (ARDEC)

$BR = AP^B$





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PAP-10-029 (ARDEC)

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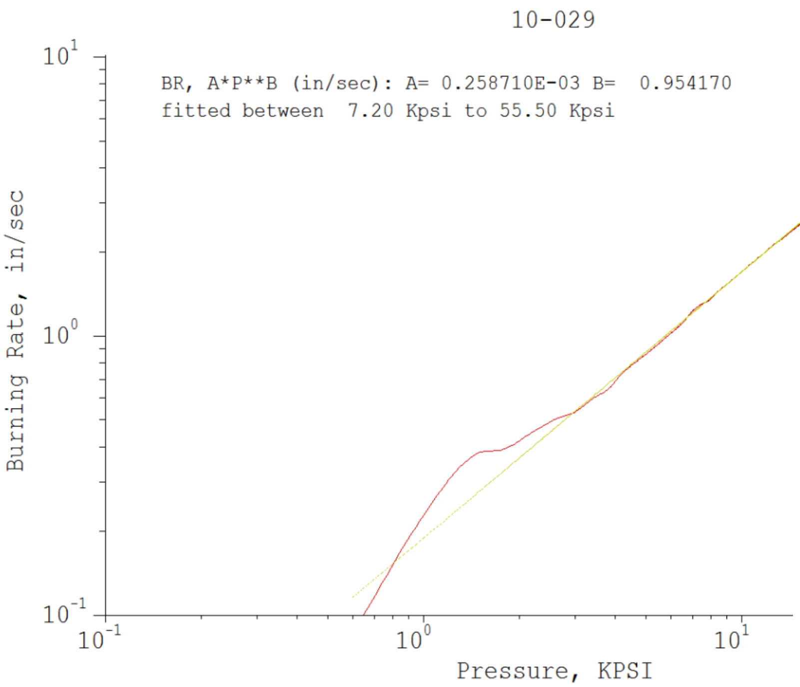
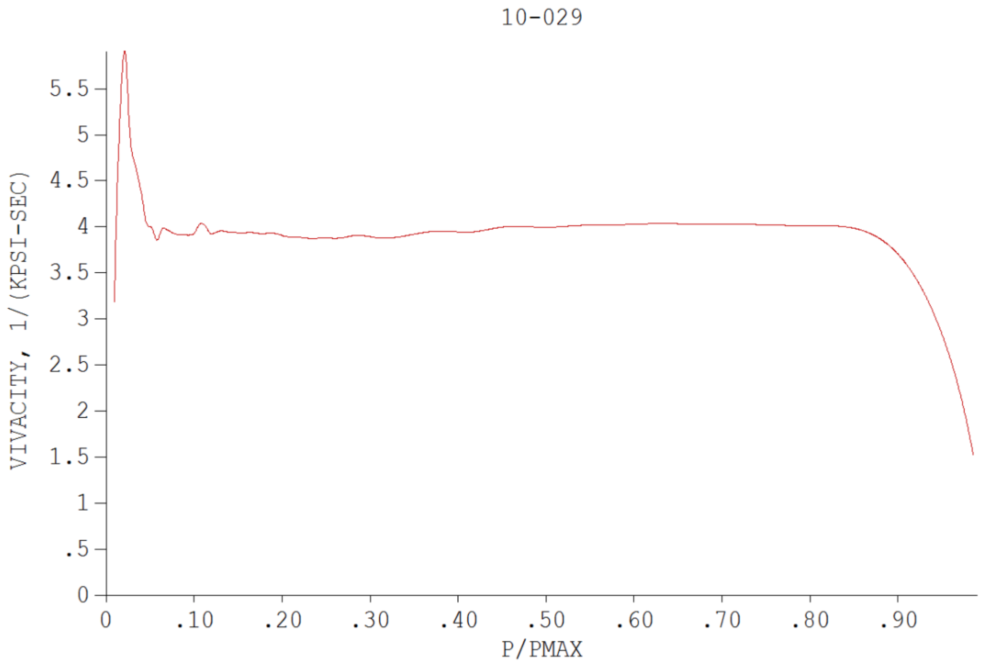
Mixing (Horizontal Sigma Blade)

Extrusion (Ram Press)

CAN, Solid Filler 1, Energetic Filler, Plasticizer A, Plastgicizer B, (Acetone/Ethyl Alcohol)

PAP-10-029 (ARDEC)





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PAP-10-065 (ARDEC)

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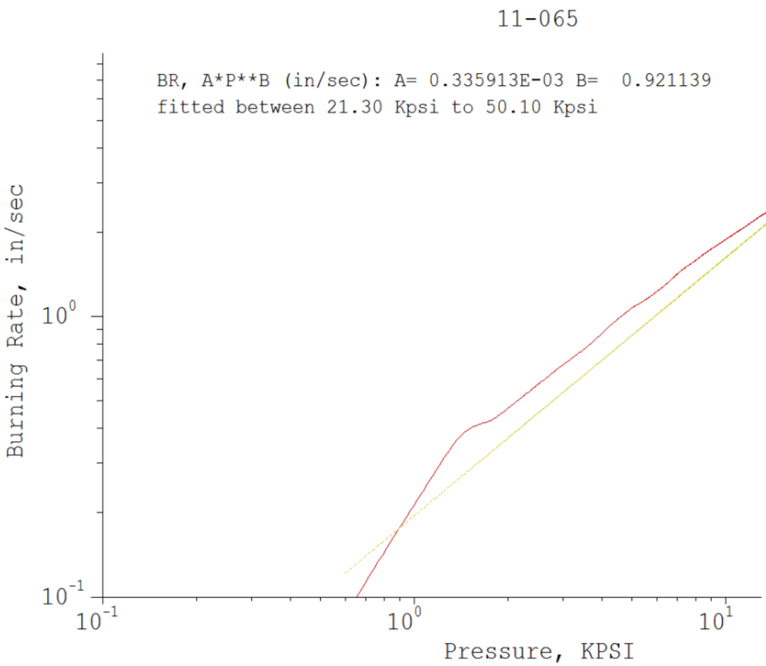

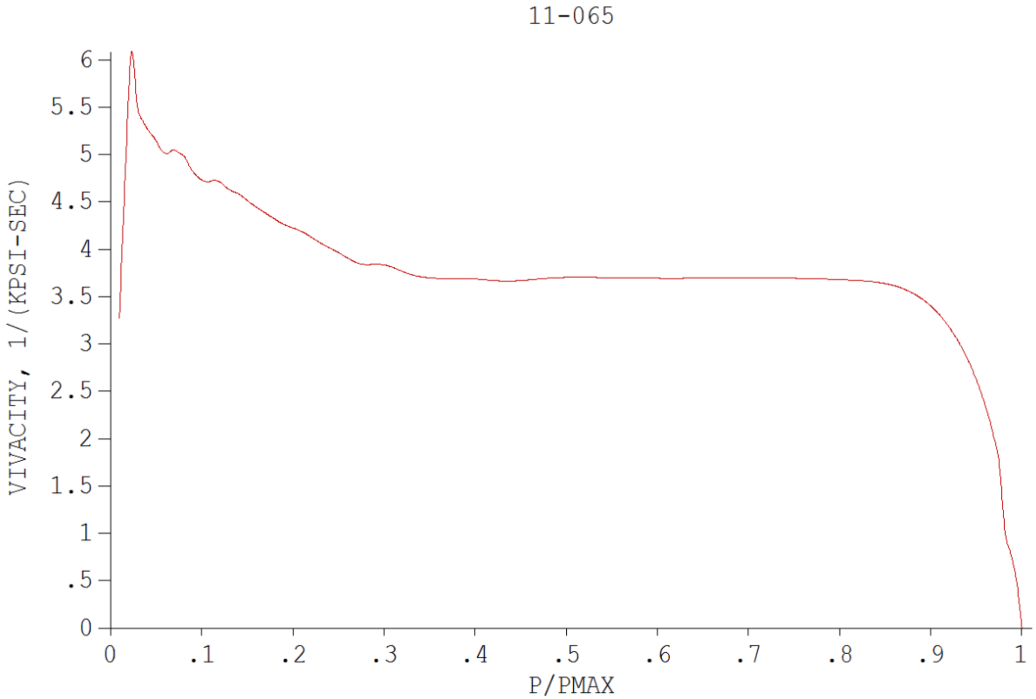

CAN, Sollid Filler, Energetic Filler Plasticizer D (Acetone/Ethyl Alcohol)

Conclusions and Recommendations

- CAN solvent solubilities different from NC.
- Propellant formulation with ground energetic filler processed well using acetone/ethyl alcohol solvent system
- CAN should be properly wetted with proper grade of alcohol to prevent propellant mixing problems.
- CAN should be dehydrated prior to shipment.

Conclusions and Recommendations (con't.)

ARDEC demonstrations to concentrate on the following

- **Gun firing to be leveraged with ARDEC ATO PROGRAM**
  - **30 mm (30mm x 173mm) Mk310 Programmable Air-Burst Munition (PABM)**
  - **105 mm (M67 and M200)**
  - **IM testing per MIL-STD-2105C**

Questions?