Industrial Perspectives on Energetic Materials

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What Are Energetic Materials?

- Energetic materials are chemicals or mixtures with a high amount of stored chemical energy. Upon initiation, they are capable of rapidly releasing a large amount of energy and gases.
- The release of energy can be initiated by impact, shock, friction, heat, flames, electrostatic discharge or electrical sparks.
- Common types of energetic materials include explosives, pyrotechnics, propellants and other fuel/oxidizer mixtures.
- Energetic materials are also referred to as high energy materials at Dow.
- In this presentation I will try to provide our perspectives on energetic materials with examples to illustrate how the hazards of energetic materials are managed at Dow.
  - Our approach is to recognize, understand and manage the hazards of energetic materials by screening, testing and hazard reviews.

Incidents Involving Energetic Materials

Consequences of high energy events (explosions) can be catastrophic!

- Hydroxylamine Explosion in Allentown, PA, Feb 19, 1999
  - 5 Fatalities, 14 injured
  - CSB Case Study of the Concept Sciences Hydroxylamine Explosion

    A process vessel containing several hundred pounds of **hydroxylamine** (HA) exploded at the Concept Sciences production facility. Employees were distilling an aqueous solution of HA and potassium sulfate. After the distillation process was shut down, the HA in the process tank and associated piping explosively decomposed, most likely due to high concentration and temperature.

- Explosions at the Port of Tianjin, China, Aug 12, 2015
  - 173 Fatalities, ~800 injured
  - Report by China's State Council Investigation Team

    Loss of the wetting agent and hot summer temperature caused **nitrocellulose** to decompose and self heat, leading to spontaneous combustion and fire, which then ignited a large quantity of **ammonium nitrate.**

Dow's Reactive Chemicals Program

- Dow's Reactive Chemicals (RC) program was established in 1966 after a tank car explosion involving a shock sensitive material.
  - Testing after the incident showed that one of the compounds can be initiated by impact.
- The purpose of the RC program is to prevent uncontrolled or unintended chemical reactions that have the potential to result in personal injury, property damage or environmental harm.
- A key element of the RC program is to understand the inherent energy in our systems and conditions under which it can be released.
- Dow is not in the business of producing explosives or energetic materials, but we may come across chemicals that contain high energy functional groups and/or may have explosive properties.
- We have developed strong capabilities to assess the hazards of chemicals and chemical processes, including energetic materials.
- The methods we use include desktop screening, calculations, testing and data interpretation, as well as hazard identification, assessment, review and mitigation.

Dow's Reactive Chemicals Capability

- **A global resource for RC consultation and testing within Dow**
- **Reactive Chemicals Subject Matter Experts (RC SME) with a wide range of expertise in RC hazard identification, assessment and mitigation**
  - Chemical reactivity, thermodynamics, reaction kinetics
  - Calorimetry, heat of reaction, thermal stability, runaway reactions
  - Gas and pressure generation
  - Chemical compatibility
  - **Energetic materials**
  - Flammability and dust explosion hazard
  - Modeling, estimations and calculations
  - Data interpretation, consultation and recommendations
  - Knowledge management, training on RC topics
- **Analysts who are highly proficient in a wide variety of calorimetry and flammability test methods**
- **RC SMEs and internal testing labs in the US, Europe and Asia**
- **External labs are used as appropriate to supplement internal testing**

Reactive Chemicals Hazard Evaluation Tools

- Over the years there have been many technological advances in screening techniques, testing methods and instrumentation for RC hazard evaluation.
- The types of testing and calculations and the amount of effort we spend will depend on the type of operation, the scale of the process, the conditions of the process, the amount of energy release, and the potential for gas and pressure generation.

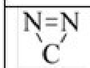
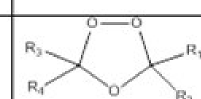
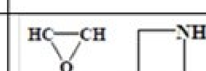
Screening, Calculations, Testing, Hazard Review

Desktop Screening for Energetic Materials

- UN Dangerous Goods Classification
  - Class 1: Explosives
    - » We want to stay away from explosives
    - » We try to avoid generation of explosives in our processes
  - Class 5.2: Organic Peroxides
    - » We do use organic peroxides in our processes
    - » We also pay attention to peroxide forming chemicals
- NFPA 704 instability/reactivity ratings 3 and 4
- High energy functional groups
- Hazard statements (R and H phrases) from MSDS
- Bretherick's Handbook of Reactive Chemical Hazards
- Chemical Reactivity Worksheet (CRW4)
- CHETAH calculations - maximum energy release from decomposition
- Yoshida's Correlation
- Safe handling guidelines from suppliers and industry trade groups
- Literature and Dow's internal database
- Lessons learned from previous incidents (inside and outside Dow)

High Energy Functional Groups

Abbreviations: **Ar** = aromatic (benzene); **M** = metal; **R** = organic chain; **X** = halogen; **Z** = anion; **n** = integer variable; all other abbreviations are for the element symbols from the periodic table of elements
Note: Not all chemical bond symbols are shown.

Functional Group(s)	Class	Functional Group(s)	Class	Functional Group(s)	Class	Functional Group(s)	Class
-C≡C-C≡C- -C≡C-C=C-	Conjugated acetylenic compounds	$H_3N \rightarrow Cr-OO-$	Aminachromium peroxocomplexes	$=N^+-N-NO_2$	N-Azolium nitroimidates	$-N-F_2$	Difluoroamino compounds
-C≡C-M	Metal acetylides	$C-N_2^+-O^-$ (ring)	Arenediazoniumolates	Ar-N=N-O-	Arenediazoates	$-C(NF)NF_2$	*N,N,N-*trifluoroalkylamidines
-C≡C-X	Haloacetylene derivatives	$-C-N_2^+S^-$	Diazonium sulfides and derivatives	ArN=N-S-A	Arenediazo aryl sulfides	NH2OH	Hydroxylamine (only compound in N-O class)
	Diazirines	N2H4 * Z, e.g. Z = HNO_3	Hydrazinium salts	Ar-N=N-O-N=N-A	Bis(arenediazo) oxides	-O-X	Hypohalites except bleach, Alkyl perchlorates, Chlorite salts, Perchlorates Perchloryl compounds Halogen oxides
-C-N=N-C	Azo compounds	$NH_4^+EO_n^-$, E=N, I, Cl	Oxosalts of nitrogenous bases	Ar-N=N-S-N=N-A	Bis(arenediazo) sulfides	M_3N	Nitrides
$R-(NO_2)_n$ for n≥2	Polynitroaryl, Polynitroalkyl Compounds	$-N^+-OH\ Z^-$	Hydroxylammonium salts	>C-N=N-N(R)-C< (R=H, -CN, -OH, -NO)	Triazenes	-R-O-O-R- R = H, C, Metal R-C(=O)-O-OH	Peroxides (cyclic, diacyl, dialkyl, etc.) Metal peroxides Hydrogen Peroxide Peroxoacids
M-N=N-R	Metal Hydrazides	$-C-N_2^+Z^-$	Diazonium carboxylates or salts	-N=N-N=N-	High-nitrogen compounds	$N=Hg^+=N-$	Poly(dimercuryimmonium salts)
$M-N_3$, $R-N_3$	Metal Azides Azides (Acyl, Halogen, Non-Metal, Organic)	$[N \rightarrow Metal]^+$ Z^-	Aminemetal oxosalts	N-N=N-N=C- (ring)	Tetrazoles	Metal-C≡N→O >C=N-O-Metal	Metal fulminates or aci-nitro salts, oximates
$F_n-Ar-Li(MgX)$ $(CF_3)_nAr-Li(MgX)$ for n = 1 - 4	Fluorinated Aryl-Li, Mg and Al Compounds	-C-N=NH	Diazeno compounds	Non-Metal- OO^- Metal-OO^- MO_2	Peroxoacids and salts Superoxides		Ozonides
R9 in contact with combustibles may cause explosion	Strong oxidizers or reducers (eg. Certain peroxides, Diazo Compounds, Nitro Compounds, Nitrites,,Nitrates, Chlorates, Perchlorates, Bromates, etc.)	R8 in contact with combustibles may cause fire	Many oxidizers or reducers eg. Potassium permanganate, nitric acid, silver nitrate, ceric ammonium nitrate, potassium nitrate, Dess-Martin reagent (periodinane), perclorates...)	$>N-NO_x$, X = 1, 2	N-Nitroso compounds N-nitro compounds	NX_3, -NX,	Nitrogen Trihalides N-halogen cmpds **NBS, NCS are fine**
				C-N triple bonds **-C≡N**	Cyano	 And other ring combinations </= 4	C1-C4 epoxides, Azetidine

Hazard Phrases for Energetic Materials

R Code	GHS Code	UN Code	Risk/Hazard Phrase
R1		EUH001	Explosive when dry
R2			Risk of explosion by shock, friction, fire or other sources of ignition
R3			Extreme risk of explosion by shock, friction, fire or other sources of ignition
R4			Forms very sensitive explosive metallic compounds
R5	H240		Heating may cause an explosion
R6		EUH006	Explosive with or without contact with air
R9			Explosive when mixed with combustible material
R16			Explosive when mixed with oxidizing substances
R19		EUH019	May form explosive peroxides
R44		EUH044	Risk of explosion if heated under confinement
	H200		Unstable explosive
	H201		Explosive; mass explosion hazard
	H202		Explosive; severe projection hazard
	H203		Explosive; fire, blast or projection hazard
	H230		May react explosively even in the absence of air
	H231		May react explosively even in the absence of air at elevated pressure and/or temperature
	H241		Heating may cause a fire or explosion
	H271		May cause fire or explosion; strong oxidizer

Bretherick's Handbook of Reactive Chemical Hazards

- **A compilation of reported reactive chemicals hazards and incidents, such as runaway reactions, fire and explosions, with references to literature**

0022. Silver nitrate
[7761-88-8] **$AgNO_3$**

Acetaldehyde
Luchs, J. K., *Photog. Sci. Eng.*, 1966, **10**, 336
Aqueous silver nitrate reacts with acetaldehyde to give explosive silver fulminate.

Acetylene and derivatives
Mellor, 1946, Vol. 5, 854
Silver nitrate (or other soluble salt) reacts with acetylene in presence of ammonia to form silver acetylide, a sensitive and powerful detonator when dry. In the absence of

Ethanol MRH 2.55/12
1. Tully, J. P., *Ind. Eng. Chem. (News Ed.)*, 1941, **19**, 250
2. Luchs, J. K., *Photog. Sci. Eng.*, 1966, **10**, 334
3. Garin, D. L. *et al.*, *J. Chem. Educ.*, 1970, **47**, 741
4. Perrin, D. D. *et al.*, *Chem. Brit.*, 1986, **22**, 1084; *Chem. Eng. News*, 1987, **65**(2), 2

Reclaimed silver nitrate crystals, damp with the alcohol used for washing, exploded violently when touched with a spatula, generating a strong smell of ethyl nitrate [1]. The explosion was attributed to formation of silver fulminate (which is produced on

Chemical Reactivity Worksheet 4.0 (CRW4)

- Co-developed by Dow, NOAA, CCPS, and others from industry and academia
- Most recent version of the tool (CRW4) can be downloaded from CCPS
- Prediction of incompatibility hazards between pairs of chemicals based on reactive groups
- Reactivity alerts
- Reactivity profile
- Reference to incidents of violent reactions or explosions when incompatible chemicals are mixed.
- CRW4 is used at Dow to generate compatibility charts
- Predictions of compatibility ratings could be too conservative in some cases
  - Verify with testing when needed

Print Chart

Export Chart Data

Chemical Pairs

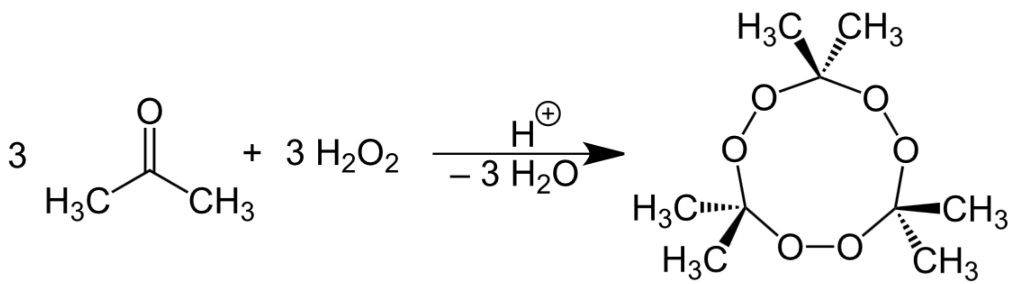
NFPA Health	NFPA Flammability	NFPA Instability	NFPA Special	Test - Compatibility Chart	ACETIC ACID, GLACIAL	ACETONE	DIPHENYLMETHANE -4,4'-DIISOCYANATE	METHANOL	PROPIONALDEHYDE	SODIUM BOROHYDRIDE	STYRENE MONOMER, STABILIZED	TOLUENE	TRIETHYLAMINE	WATER
3	2	0		ACETIC ACID, GLACIAL										
1	3	0		ACETONE	Y									
				DIPHENYLMETHANE -4,4'-DIISOCYANATE	N	Y								
1	3	0		METHANOL	C	C	N							
2	3	2		PROPIONALDEHYDE	N	C	C	C	SR					
				SODIUM BOROHYDRIDE	N	N	C	N	N					
2	3	2		STYRENE MONOMER, STABILIZED	C	C	C	C	N	N	SR			
2	3	0		TOLUENE	Y	Y	Y	Y	Y	Y	Y			
3	3	0		TRIETHYLAMINE	N	Y	N	Y	N	N	N	Y		
				WATER	Y	Y	N	Y	C	N	C	Y	C	

Mixing Incompatible Chemicals

DOW

Examples of mixing incompatible chemicals that could produce explosives

- Mixing acetone with H_2O_2 will produce tri-cyclic acetone peroxide (TATP).



- Solution of Ag_2O in NH_4OH exploded – formation of silver nitride.

$$3\ Ag_2O + 2\ NH_3\ (aq) \longrightarrow 2\ Ag_3N + 5\ H_2O$$

- Mixing an acidic solution of silver nitrate with alcohol will produce silver fulminate.

$$AgNO_3 + ROH\ (alcohol) \longrightarrow AgCNO\ (silver\ fulminate)$$

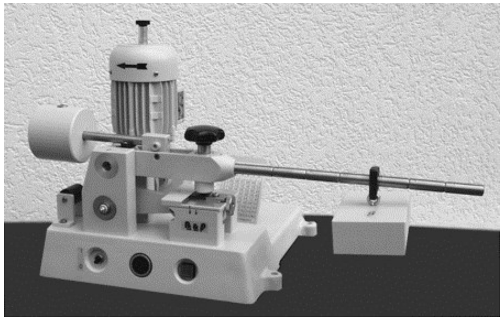
- Passing acetylene gas through copper(I) chloride solution will produce copper acetylide.
- Acetylene gas can form explosive compounds if it comes in contact with silver, copper or mercury.
    - Copper pipes cannot be used for acetylene gas.

Formalized and Documented Hazard Reviews

- **An essential aspect of a strong Reactive Chemicals Program involves formalized and documented hazard reviews**
  - Management of Change (MOC)
  - Facility Reactive Chemicals/Process Hazard Analysis (RC/PHA)
  - Reactive Chemicals/Laboratory Hazard Analysis (RC/LHA)
  - Project RC/PHA
  - New Leader Reviews (NLR)
- **Multi-disciplinary review teams with broad functional representation, technical expertise and backgrounds**
- **Checklists and questions about energetic and reactive materials**
  - Highly reactive or explosive materials
  - Pyrophoric and water reactive materials
  - Shock and friction sensitive materials
  - Self-reactive, time-sensitive and temperature-sensitive chemicals
  - Peroxides and peroxide forming chemicals
  - Silicon hydride (SiH) containing materials
  - Strong oxidizers (may cause fire or explosion)

Energetic Materials Testing

- **Internal testing capabilities**
  - Thermal screening and thermal stability testing
    - » Differential Scanning Calorimetry (DSC)
    - » Thermal Screening Unit (TSU)
    - » Accelerating Rate Calorimetry (ARC)
  - Impact sensitivity (drop weight test)
- **Work with external labs on UN/DOT explosivity testing for transportation classification**
  - At Dow, we rarely need to test explosivity for transportation classification
  - Impact sensitivity
  - Friction sensitivity
  - Card gap tests
  - Koenen tube tests
  - Time/pressure tests

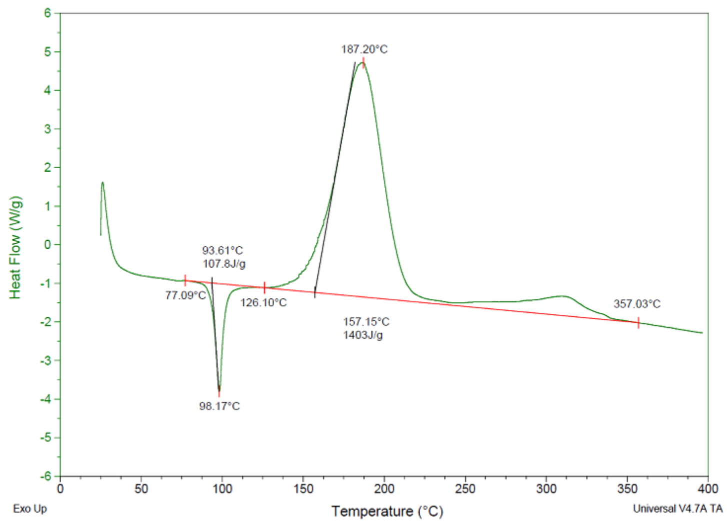


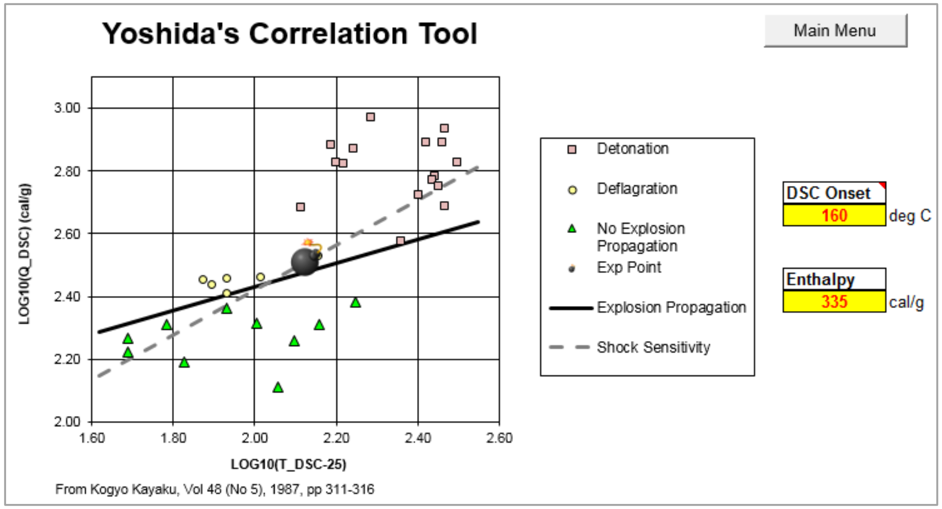
BAM Friction Apparatus

BAM Fallhammer

Example – Sulfonyl Azide Compound

- **Thermal stability by DSC**
- **Yoshida's Correlation**
  - A screening tool for potential explosivity and impact sensitivity hazards by DSC
  - Strictly empirical method derived from a series of tests on known high energy materials in the powder form, mainly nitro compounds
  - Predicts a material's hazard potential when subjected to low-to-moderate energy forces

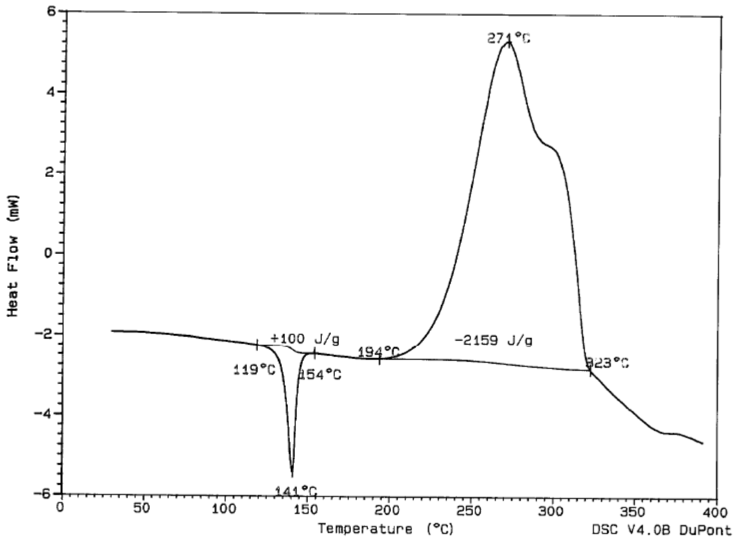


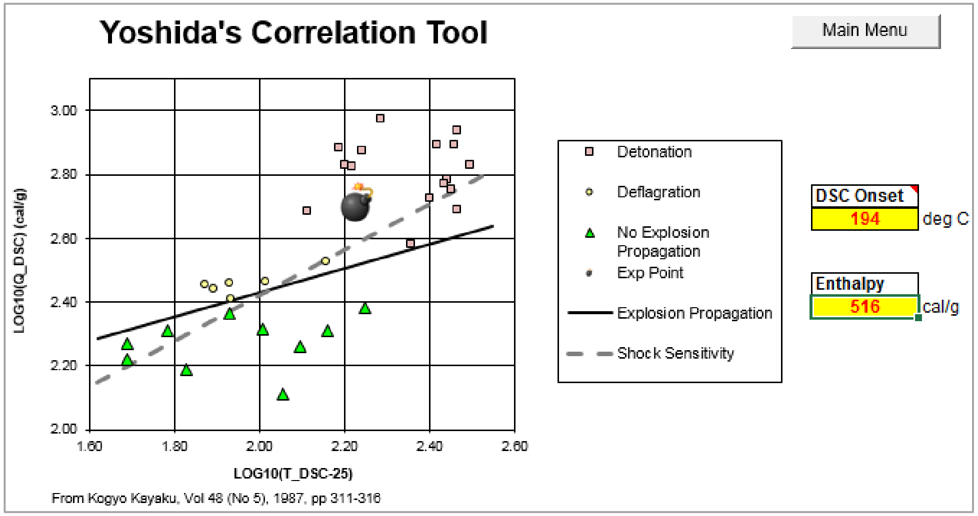


- **Impact sensitivity testing by BAM Fallhammer**
  - Ignition energy: 30-40 J (not very sensitive)

Compound: Dinitroaniline Derivative

- DSC, onset: 194°C, energy: -2159 J/g
  - Sealed glass capillary under N_2
  - Inert and resistant to corrosion (except caustic and HF solutions)
  - No pressure measurement





- ARC, onset: 161°C, energy: -2227 J/g, max pressure: 540 psia
  - Measures heat (exotherm only) and pressure under adiabatic conditions
  - Sample size: 0.48 g (Phi = 8.64)
  - ARC pre-task checklist includes questions about high energy functional groups and measured energy from DSC. Limit sample size to <0.5-1 g if energy >1000 J/g.

Compound: Dinitroaniline Derivative

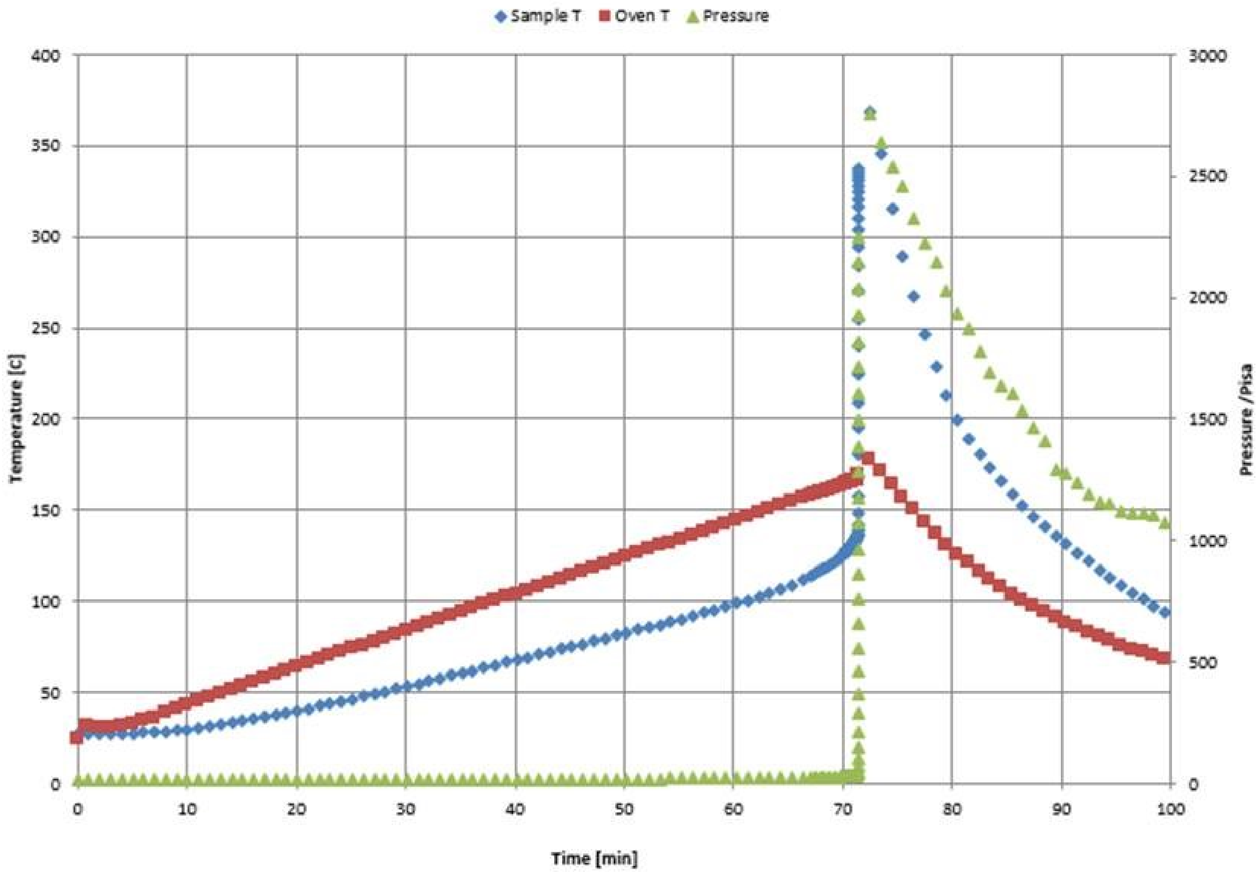
- **Explosivity testing for transportation classification by external lab**

Test	Observation	Pass (-) / Fail (+)
UN Test Series 1(a), Card Gap, Zero Gap	Plate bent, undisturbed pipe and some materials left on the plate on all 3 test trials	Pass (-)
UN Test Series 1(b), Koenen	Type "F" response, tube fragmented into 3 or more; at 2.0 mm and 3.0 mm diameter orifice. Note: Orifice tends to plug up with this material	Fail (+)
UN Test Series 2(b), Koenen	Type "F" response, tube fragmented into 3 or more; at 2.0 mm and 3.0 mm diameter orifice. Note: Orifice tends to plug up with this material	Fail (+)
UN Test Series 1(c)(i), Time/Pressure	Max pressure recorded >350 psi (>2070 kPa)	Fail (+)
UN Test Series 2(c)(i), Time/Pressure	No-go, material exhibited explosive character but not sufficient to be classified as an explosive by this test	Pass (-)
UN Series 3(d), Small scale burn test	Sample burned, no ignition	Pass (-)
UN Series 3(a)(i) Bureau of Explosives impact machine	No smoke, flame or ignition in 10 trials at 10 cm drop height	Pass (-)
UN Series 3(b)(i) BAM Friction apparatus	No ignition in six trials at 360 N	Pass (-)

- **Expert recommendations: based on the testing results, the substance should not be classified as an explosive for transportation.**

Example – Thermal Screening by TSU

- **A simple, fast way to generate pressure and thermal onset information**
  - Thermocouple in the sample, but heat data is not quantitative (not adiabatic)
- **TSU detected a decomposition with very rapid temperature and pressure rise**

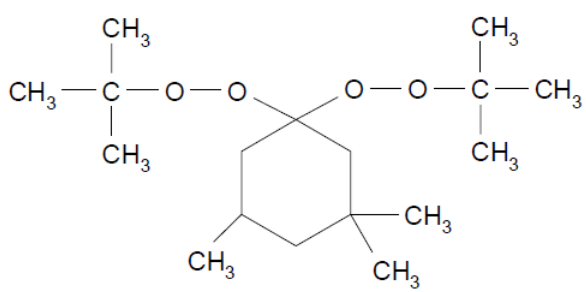


Free Radical Initiators for Polymerization

- These are mostly organic peroxides and azo compounds.
- By design these initiators will decompose at the process temperature to produce free radicals that will catalyze polymerization reactions.
- Some have relatively low SADT and require storage at low temperatures
- Some may be sensitive to shock and friction

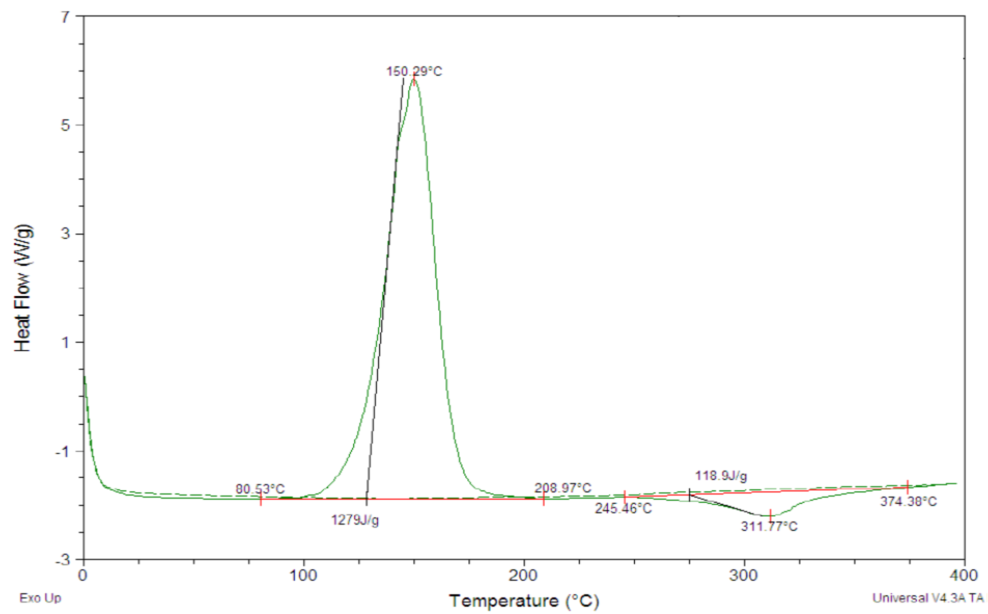
Trigonox 29

1,1-Di(tert-butylperoxy)-3,3,5-trimethylcyclohexane



From supplier

- SADT: 60°C
- Storage: below 25°C
- Shock and friction sensitive



Peroxide-Forming Chemicals

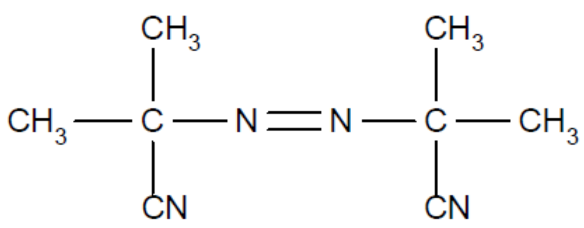
- List A: chemicals that form explosive levels of peroxides without concentration.
  - Example: divinyl acetylene, divinyl ether, isopropyl ether
- List B: chemicals that form explosive levels of peroxides upon concentration (distilled, evaporated or otherwise concentrated).
  - Example: tetrahydrofuran (THF), diethyl ether, methyl acetylene
- List C: chemicals that may polymerize as a result of peroxide accumulation.
  - Example: styrene, acrylonitrile, vinyl acetate
- List D: chemicals that may form peroxides but cannot be clearly placed in List A, B or C.
- Safe handling of peroxide-forming chemicals
  - Store peroxide-forming chemicals in tightly sealed and light-resistant containers, away from heat, direct sunlight and sources of ignition
  - Inert gas can be introduced as a blanket to minimize available oxygen
  - Inhibit with antioxidants (for example, THF inhibited with 250 ppm BHT)
  - Adhere to recommendations about shelf-life and testing schedule
  - Do not touch or attempt to open container of a peroxide-forming liquid if there are crystals around the cap and/or in the bottle

Near-Miss Incident Involving AIBN

- Solution of AIBN stored at room temperature by mistake in a R&D lab
- Generation of N_2 gas over time due to decomposition of the azo compound
- The solution ejected from the bottle when trying to open the bottle
- Recommended storage temperature: 2-8°C (refrigerator)
- Calculated half-life: 22 years at 5°C; 6 months at 25°C

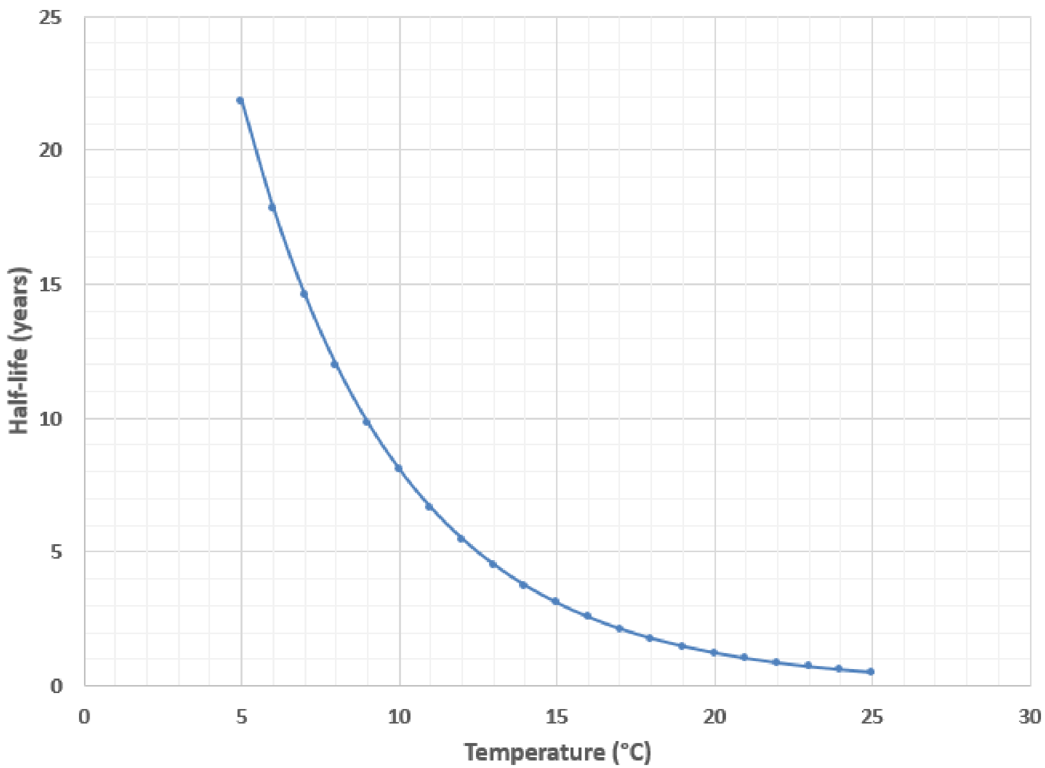
AIBN

Azobisisobutyronitrile



DSC data

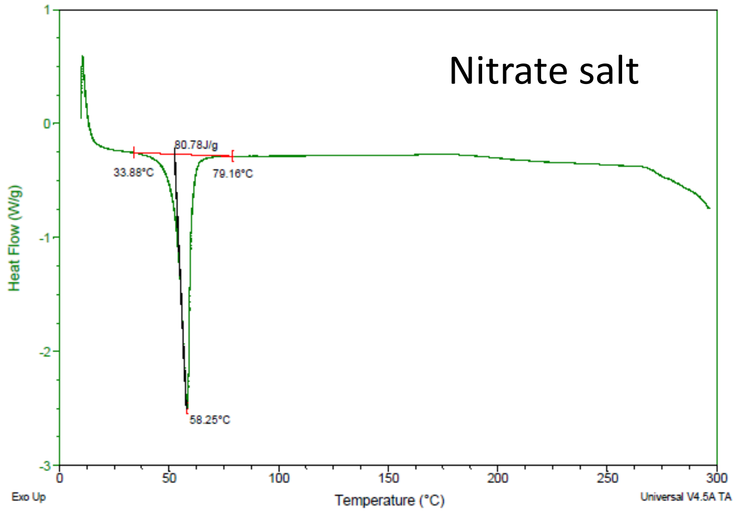
- 20% AIBN in chloroform
- Onset temperature: 60°C
- Energy: -1360 J/g AIBN

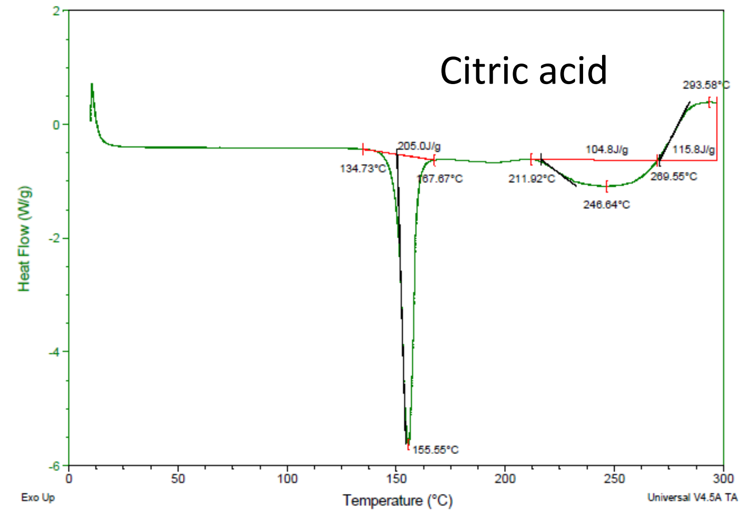


Example – MOC Review

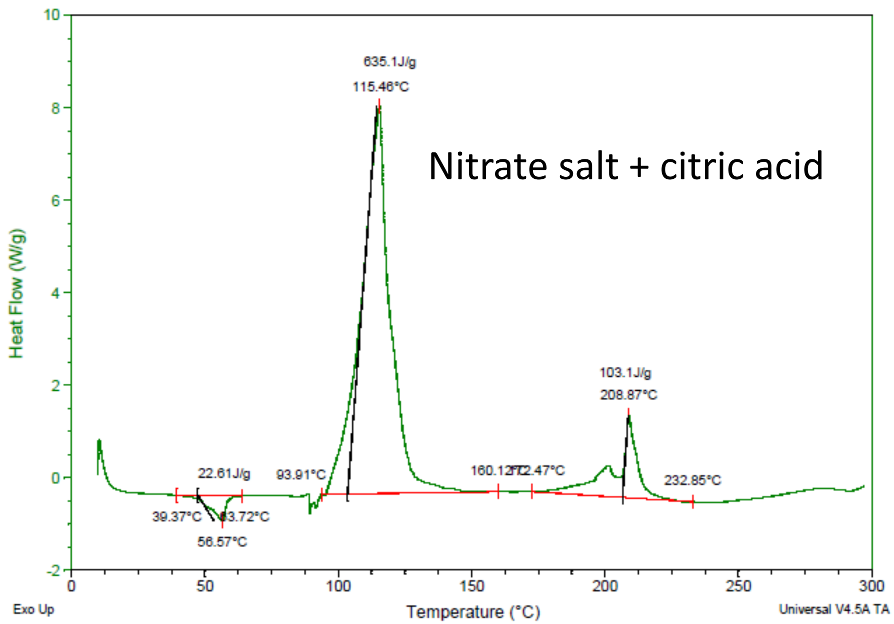
- A researcher planned to run small-scale synthesis reactions in a R&D lab.
- The reaction is between a nitrate salt and urea or citric acid.
- Neat reaction (no solvent) in molten state
  - Melting points: nitrate salt: 57°C; urea: 132-135°C; citric acid: 156°C
- Planned reaction conditions: temperatures up to 150°C and ambient pressure
- MSDS for the nitrate salt: hazard phrase H272 (may intensify fire; oxidizer)
  - H272 in MOC trigger grid requires Reactive Chemicals review.
- Urea will decompose at elevated temperatures to generate CO_2 and NH_3.
- Citric acid will decompose at elevated temperatures to generate CO_2.
- RC SME suggested DSC and ARC tests to help to answer some of the questions about safe operation of the experiments, such as heat generation, onset temperature, reaction kinetics, side reactions, and gas generation.
- Conclusions based on test results:
  - The reaction between nitrate salt and urea is safe to run (mild heat and gas generation).
  - The reaction between nitrate salt and citric acid is not safe due to very rapid heat and gas generation.
- This example illustrated the importance of following the MOC trigger grid in preventing potential incident.

Example – MOC Review



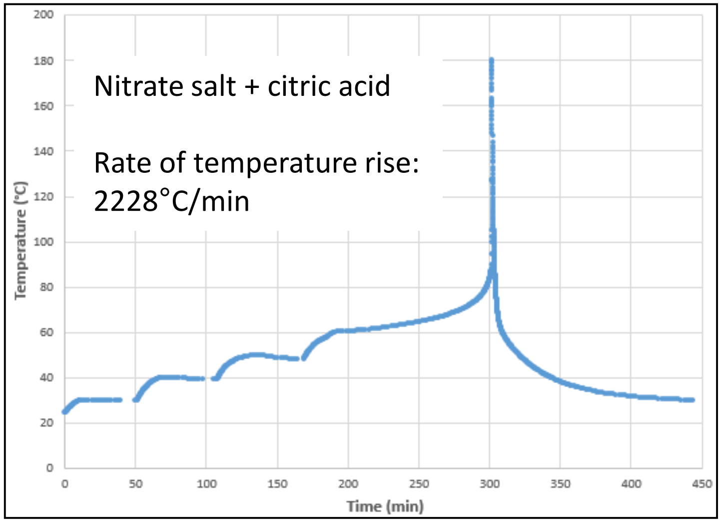


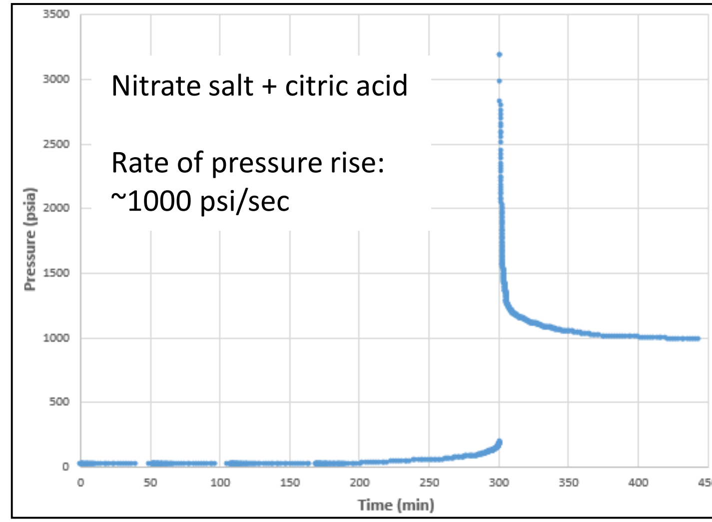
DSC

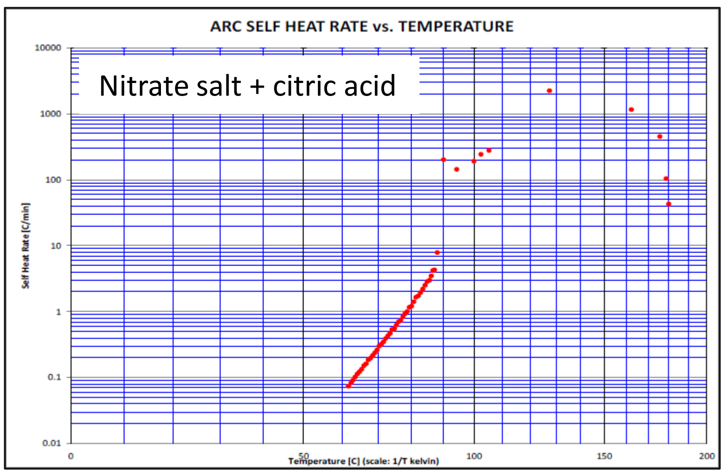


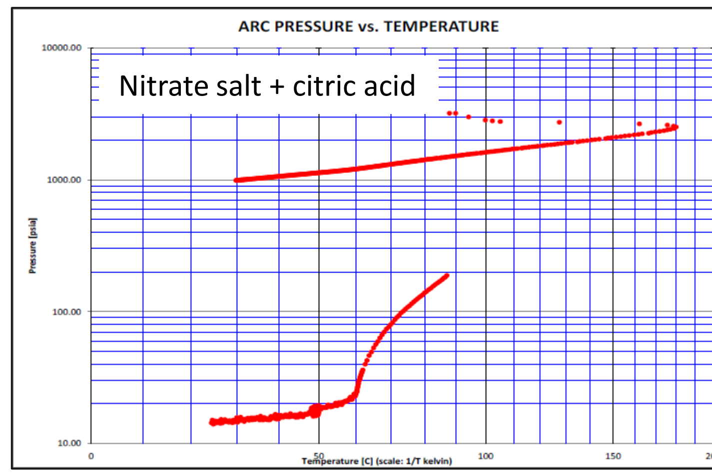
Example – MOC Review

ARC





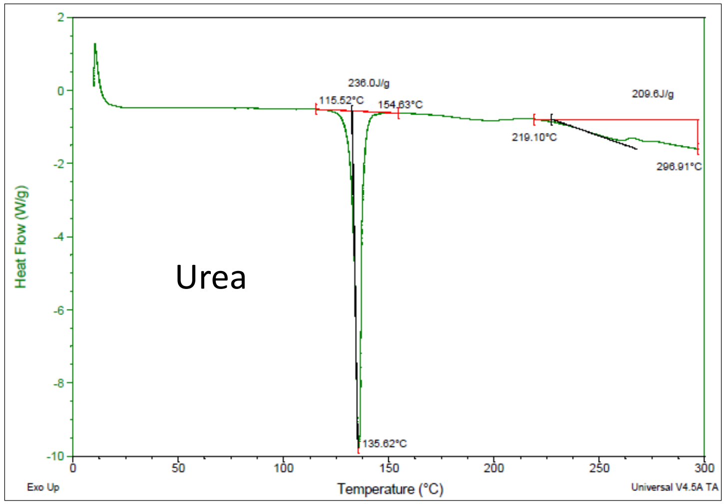


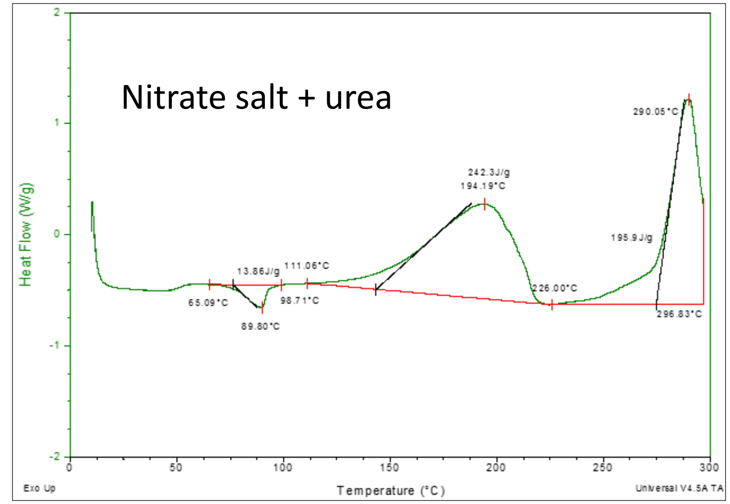


Because of the sudden release of energy and gases and rapid increase in temperature and pressure, it is not safe to run the reaction between the nitrate salt and citric acid.

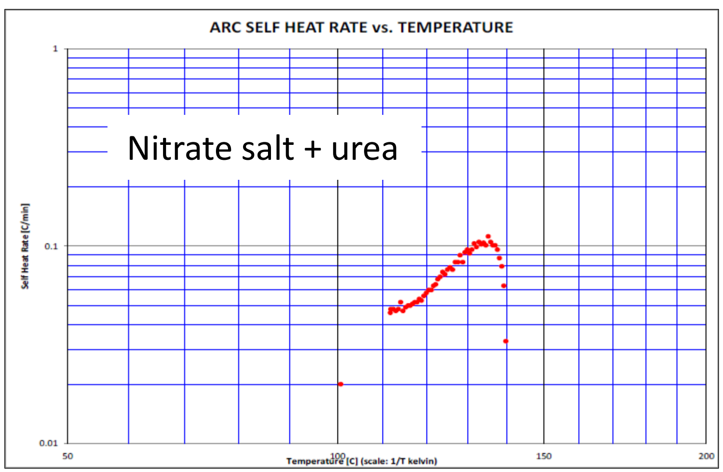
Example – MOC Review

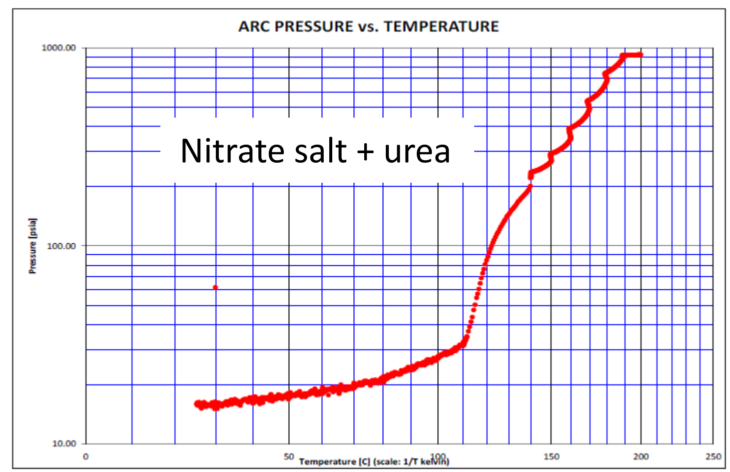
DSC





ARC





The tests showed mild and slower heat and gas generation. It is safe to run the reaction between the nitrate salt and urea.

Concluding Remarks

- Dow continues to be a strong leader in Process Safety (PS) and Reactive Chemicals (RC) to advance best practices and develop new technologies for identifying and managing process hazard risks.
- Dow is not in the business of producing explosives or energetic materials, but we may come across chemicals that contain high energy functional groups and/or may have explosive properties.
- A key element of Dow's RC program is to understand the inherent energy in our systems and conditions under which it can be released.
- Our approach to energetic materials is to recognize, understand and manage the hazards by screening, testing and hazard reviews.
- Our intent is that by sharing Dow's practices for identification, assessment and management of reactive chemicals hazards, the chemical process industries can realize benefits from improved safety performance and reliability of operations, fewer incidents over the life of a process, and reduced consequences of any incidents that may occur.

THANK YOU!

Questions?