

CHEMICAL COMPATIBILITY AND SAFE STORAGE CONSIDERATIONS FOR  
PROCESS SYSTEMS HAZARDS ANALYSIS

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**ABSTRACT**

An approach to evaluating the Chemical Compatibility and Safe Storage aspects of Process Systems Hazards Analysis has been delineated.

Differential Scanning Calorimetry/Thermal Gravimetric Analysis techniques have been utilized to evaluate potential Chemical Compatibility in storage hazards with chemicals in contact with explosives and propellants. Utilization of the Frank-Kamenetski developed equations was made to determine the safe storage criteria for chemicals and chemicals in contact with contaminants. Special attention was given to Nitrocellulose materials.

**INTRODUCTION**

Chemical Compatibility Hazards arise in two major areas of propellants/explosives/pyrotechnic manufacturing and use. The first is in the in-process operations of manufacture. Here the particular chemicals can come in contact with contaminants, adhesives, greases, and other foreign chemicals. The second critical area is that of storage of materials once they have been manufactured and/or placed in the item configurations.

Chemical Compatibility problems of in-process operations usually are minimized by thorough quality control and inspection methods. An upset in the Process System may create some severe Chemical Compatibility Hazards if people are not aware of the effects of various chemicals on the propellants/explosives/pyrotechnics and their intermediary configurations during the processes. Normally, these potential hazards are uncovered by Systems Hazards Analysis such as Failure Modes and Effects Analysis and Fault Tree Analysis. Through these type of Analyses, identification of critical contacts of in-process chemicals can be made. We know basically that liquids in a chemical process are of much more concern than solids because they can be contaminated very easily by gases, liquids and other solids. The chemical reactions of these contacts can range from complete inaction to very violent reactions. In some cases, an explosive mixture can be formed when the combinations of chemicals under right conditions occur.

In storage, another set of problems arise. Here we have the remote possibility of migration of chemicals (by no means as likely as in the in-process configuration). In storage, we must be concerned about the long-term effects on the explosives, propellants

and pyrotechnics. Decomposition of the materials can occur and self-heating will result. Biological degradation of the materials can also occur. Normally, sufficient information is known about the propellants, explosives and pyrotechnics to evaluate their storage capabilities. Occasionally in storage, a synergistic effect can occur when other chemicals come in contact with the basic materials. These contaminants can make contact with the materials during the in-process handling, transportation and shipment and in storage with other chemicals. Depending on the storage configurations, heating of the buildings and facilities can occur during the hot months of the summer. High relative humidities can also promote biological degradation, rusting and other actions which could contribute as catalysts to a decomposition process.

In both cases (storage and in-process), we must be concerned about the effects of chemicals and contaminants on the base materials. The incompatibilities can arise and affect the following properties of the material:

- Initiation Sensitivity
- Flame or Explosion Propagation Characteristics
- Formation of Toxic, Flammable or Carcinogenic Gases or Liquids
- Self-heating Accelerations

In some cases, the incompatibility can generate excessive corrosion and mechanical effects to create a potential handling hazard of an end item. For instance, the base of a projectile corrodes out and exposes a booster charge to the elements.

In the past, chemical compatibility with an explosive, pyrotechnic or propellant was found by using a Differential Scanning Calorimeter to monitor changes in ignition onset temperatures or lower temperature exotherm reactions.

In this Paper, we review an approach which delves much deeper into the compatibility type problem.

## APPROACH

Once a number of chemicals have been identified which could potentially come in contact with a propellant, explosive or pyrotechnic, the analyst must decide which of these can be most hazardous. In our past experience, we have found that the Differential Scanning Calorimeter is a good tool for screening through the various chemicals which could come in contact with the basic materials. Here, we mix a mixture of the explosive, propellant or pyrotechnic with a contaminating chemical. After sufficient storage time, Differential Scanning Calorimetry scans are made at scanning rates normally 10 or 20 degrees centigrade per minute. If a reduction in exothermic onset temperature by greater than 10 degrees is noted, a Thermal Gravimetric Analysis plot is made on the same materials. A typical Differential Scanning Calorimeter Exothermic Curve for Nitrocellulose is shown in Figure 1. Several tests are usually run on a chemical which could come in contact with the in-process material, so that all potential methods of contact can be explored. For instance, adding water plus the chemical plus a propellant may be done to determine the effects of water on the process.

Once an incompatibility has been identified on the Differential Scanning Calorimeter and the Thermal Gravimetric Analyser, further testing and evaluation is necessary.

The next step is that of determining the Arrhenius Kinetic Constants of the in-process material/contaminating chemical. Activation energies of first exothermic reactions plus frequency values are determined by using Differential Thermal methods. Normally, from a compatibility standpoint, we are most concerned about the early stages of decomposition and how this accelerates to yield a self-heating and a runaway reaction. At the present time, the ASTM E-27.02 Committee has drafted a test method for determining the Arrhenius Kinetic Constants. Hopefully, this Standard will be forthcoming so that everyone in the industry can utilize a common method.

Once the Arrhenius Kinetic Constants have been defined for the chemical contaminants and in-process material combination, further review must be made to be certain that the chemical reaction mechanisms observed in the Differential Scanning Calorimeter are truly indicative of those that would be expected in process. For instance, the chemical reaction may occur without presence of air. If there is a possibility that air may be present, the Differential Scanning Calorimetry tests should also utilize air and other gas combinations expected. Decisions need to be made to determine whether the materials shall be run on the Differential Scanning Calorimeter in the sealed containers or open containers.

By utilizing the Frank-Kamenetski developed equations for determining critical temperature for runaway reactions as follows:

$$T_m = \frac{E}{2.303 R \log \left( \frac{\rho a^2 Q Z E}{\lambda R T_m^2 \delta} \right)} \quad (1)$$

where:

- E - Activation Energy (Kcal/mol)
- R - Univ. Gas Constant
- $\rho$  - Material Density (gm/cc)
- a - Slab Half Thickness, Cylinder or Sphere Radius (cm)
- Q - Heat of Reaction (cal/gm)
- Z - Arrhenius Freq. Factor (Sec<sup>-1</sup>)
- $\lambda$  - Heat Transfer Coeff. (cal/cm-sec<sup>o</sup>K)
- T<sub>m</sub> - Critical Self-Heating Temp. (°K)
- $\delta$  - F-K Shape Factor
  - For Slab  $\delta = 0.88$
  - For Cylinder  $\delta = 2.00$
  - For Sphere  $\delta = 3.32$

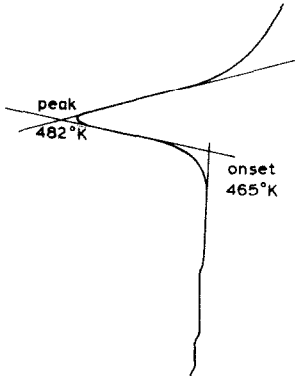


FIGURE 1 - TYPICAL DCS EXOTHERM CURVE FOR NITROCELLULOSE

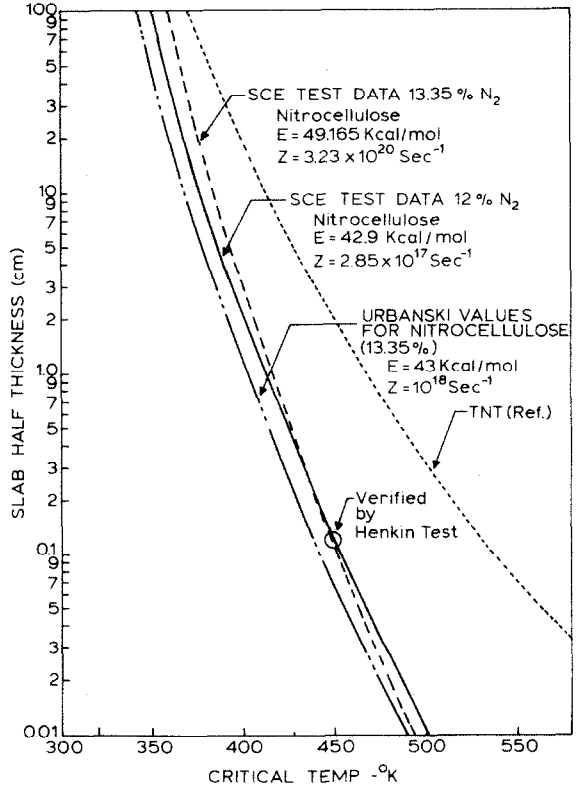


FIGURE 2 - CRITICAL TEMPERATURE FOR RUNAWAY REACTION IN SLAB FOR NITROCELLULOSE (Using Various Arrhenius Kinetic Constant Data)

We can determine the critical temperature for runaway reaction based on a configuration of the in-process or stored materials.

Recently we have evaluated Nitrocellulose configurations to determine their compatibility in in-process material handling. We have found numerous data on the reaction kinetics of Nitrocellulose. A summary of the kinetics and thermodynamics properties of Nitrocellulose, Nitroglycerine and other explosive materials are found in Table I. Since there was a wide disparity in the values of activation energy and frequency factor, we have run tests to determine the values for two Nitrocellulose type materials. A 12% Nitrogen/Nitrocellulose and a 13.35% Nitrogen/Nitrocellulose material was tested to determine the Arrhenius Kinetic Constants so that we could determine the safe storage temperatures of these in-process materials.

Critical temperature for runaway reactions for slabs of Nitrocellulose were calculated based on Equation (1) and are shown in Figure 2. In this Figure, we also list the Arrhenius rate

**TABLE I - KINETICS AND THERMODYNAMIC PROPERTIES OF PROPELLANTS AND EXPLOSIVES**

<u>MATERIAL</u>	<u>Activation Energy E (Kcal/mil)</u>	<u>Frequency Factor (1/sec)</u>	<u>Density (gm/cc)</u>	<u>Specific Heat (cal/gm°C)</u>	<u>Thermal Conductivity (cal/sec-cm°C)</u>	<u>Ons Ign Tem (°C)</u>
Nitroglycerin (20-125°C) (140-150°C)	+48	+10 <sup>20.8</sup>	1.586	+0.30	+0.000503	210'
	U <sub>42.6</sub>	U <sub>10<sup>20</sup></sub>				
	U <sub>45</sub>	*10 <sup>14</sup>				
	*35	*10 <sup>18</sup>				
	s <sub>42.6</sub>	s <sub>10<sup>19.2</sup></sub>				
(80-125)	s <sub>45.0</sub>	s <sub>10<sup>23.5</sup></sub>				
(125-150)	s <sub>50.0</sub>					
(150-190)						
Nitrocellulose (13.15N) (126-156°C)	46.2	10 <sup>24.68</sup>		E <sub>0.34</sub>	E <sub>.00051</sub>	200
	U <sub>43</sub>	U <sub>10<sup>18</sup></sub>				
	s <sub>49</sub>	s <sub>10<sup>21</sup></sub>				
	s <sub>48</sub>	s <sub>10<sup>20</sup></sub>				
	s <sub>48</sub>	s <sub>10<sup>24</sup></sub>				
	s <sub>56</sub>	E <sub>1.34x10<sup>16</sup></sub>				
	E <sub>41.2</sub>	E <sub>10<sup>19</sup></sub>				
(205-270)	E <sub>46.7</sub>					
(130-155)						
PEIN (100-120°C)	+38.6	+10 <sup>15.3</sup>	+1.46	+0.272	+0.0006	225
	s <sub>50.9</sub>	s <sub>10<sup>20.6</sup></sub>	—	—	—	
HMX (170-200)	+57.2	+10 <sup>21.2</sup>	E <sub>+1.66</sub>	E <sub>0.264</sub>	E <sub>+0.00049</sub>	260
	E <sub>57.2</sub>	E <sub>2.1x10<sup>24</sup></sub>				
HMX	+57.2	+5x10 <sup>19</sup>	+1.66	+0.315	+0.00049	327
TNT (200-260) (257-310)	E <sub>37.0</sub>	E <sub>5x10<sup>13</sup></sub>	E <sub>1.57</sub>	E <sub>0.264</sub>	E <sub>0.00046</sub>	427
	*34.4 (L)	E <sub>10<sup>11.4</sup></sub> (L)				
NM	*49.2	*10 <sup>13.7</sup>	*1.14	0.412	.00051	370

**SUPERSCRIPT SYMBOLS**

- \* Russian Data - JPRS, 47,007- 4 Dec. 1968
- + Picatinny Tech. RPT 3157, June 1964
- s Solid Propellant Rockets, Princeton Univ. Press
- U Urbanski, Chem. & Tech. of Expl.
- E Erosive Burning - Solid Propellants

parameters calculated at our facility. We also plotted on the same Figure, the critical temperature for runaway for Nitrocellulose using Urbanski's Rate Kinetics Constants.

Calculations of the explosion times for runaway reactions based on various surface temperatures should be calculated next. We have done this for the Nitrocellulose materials which is illustrated in Figure 3. Published data for TNT was used to determine critical temperature and time to explosion as reference. The explosion temperature was calculated by using the following equation:

$$t_{\text{exp}} = \frac{\int C_p a^2}{\lambda} F (E/T_m - E/T_i)$$

where:

$C_p$  - Specific Heat (cal/gm<sup>o</sup>K)

$a$  - Slab Half Thickness  
(cm)

$T_m$  - Critical Temp (<sup>o</sup>K)

$T_i$  - Surface Temp (<sup>o</sup>K)

$F$  - Function of Geometry

Ref: "Thermal Initiation of  
Explosives"

J. Zinn, C. Mader

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After time to explosion calculations are made based on surface temperature slab, subscale tests are usually run to verify that the chemical kinetics data and time to explosion temperature data is valid. We normally run a Henkin Test (Reference: E. Henkin and R. McGill, Ind. Eng. Chem., 44, 1391 (1952)). Here a known quantity of chemical is placed in a copper containment vessel and sealed against pressure. The sample is then placed in a Woods Metal Bath at a given temperature and the time is monitored until explosion occurs. As we see in Figure 3, we ran three Henkin Test Data Points to determine the time to explosion. We found that the time to explosion values came very close to the values calculated by using a slab half thickness of 0.12 centimeters (which was utilized in the Henkin Test). Actually, the Urbanski supplied information on chemical kinetics does not yield good time to explosion or critical temperature for runaway data for Nitrocellulose. After completion of the Henkin Tests, decisions are then made to determine the adequacy of analytical and test data in relation to the applications of the explosive chemical contaminant type systems.

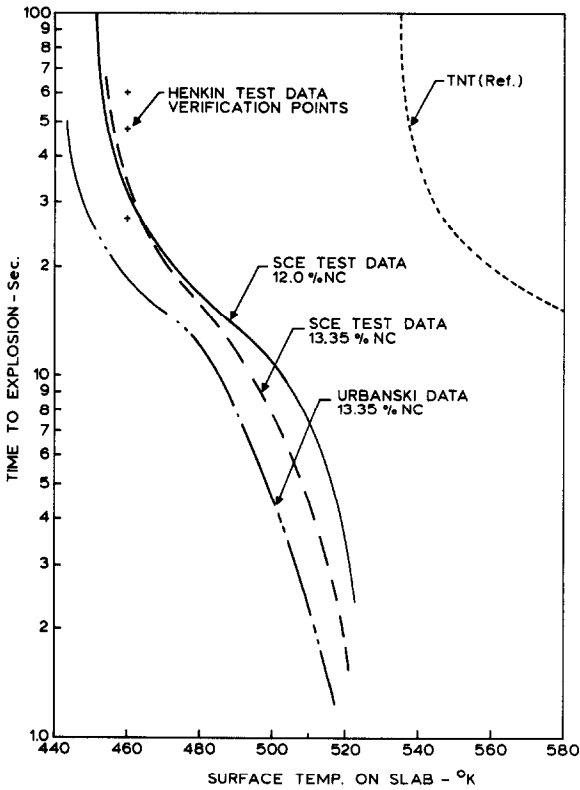


FIGURE 3 - COMPUTED EXPLOSION TIMES FOR SLAB OF HALF THICKNESS,  $a = 0.12$  cm (Using Various Arrhenius Kinetic Constant Data For Nitrocellulose)

### CONCLUSIONS AND RECOMMENDATIONS

We have presented an approach to evaluate the chemical compatibility of in-process and stored materials. Calculations of safe storage temperature and sizes can be readily made on a routine basis. Verifications of the results normally should be made on subscale size quantities to be sure that scaling does apply. We did find in our testing of the Nitrocellulose materials that the Urbanski data on 13.35% Nitrocellulose did not yield accurate time to explosion and critical temperatures.