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Tektronix Component Solutions

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Advanced Pyrotechnics 2: Ignition, Sensitivity, and Analysis of Energetic Materials

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Advanced Pyrotechnics 2:
Ignition, Sensitivity, and Analysis of Energetic Materials

DON'T MOVE, or I'll fill you full of 98% lead, 1% antimony, 0.75% silver, 200 parts per million nickel, trace amounts of cobalt, and other components below their respective detection limits!

Wait a minute! Are these values CERTIFIED??!

Analytical Chemists in the Wild West

Chris Mocella
ACS Webinar, June 2015
Review: Basics of Pyrotechnics

- Oxygen source (oxidizer) + electron source (fuel) → Products + Energy
- Energy Output =
  - Light (color)
  - Sound
  - Pressure
  - Motion
  - “The effect”

Ingredients for Pyrotechnic Mixes

- **Oxidizing Agents** (oxygen rich, occasionally fluorine)
- **Fuels** (organic, metallic, other)
- **Color ingredient**
- **Intensifier**
- **Binder** (small %, can also act as a fuel)

- Charcoal + KNO₃ + Sulfur = Black Powder
- Light a match → CO₂, H₂O, K₂O, N₂, SO₂, “soot”, and **ENERGY!**
Principles of Ignition

- **Ignition**: The ability to ignite/initiate the material using an external stimulus (with respect for stability of the material in the absence of the stimulus)
- For ignition to occur, a material must be heated to its ignition temperature, where the reaction will initiate and propagate
- The stimulus can be heat or flame, spark, as well as friction or impact, or some manner of transferring energy from the stimulus to the material, heating the chemicals
- What happens when sufficient stimulus is applied?

Ignition: Complexity and Propagation

- Upon sufficient stimulus, the materials will undergo a complex sequence of events, such as crystalline changes, melting, boiling, decomposition, interaction of liquid/vapor phases or fleeting decomposition products.
- These complex products and interactions take place on the materials and also in any visible flame.
- If the necessary activation energy has been applied, the reactions occur, more heat is evolved to give stimulus to unreacted material, propagating the reaction.
**Ignition: Physical States**

- **Requirement for ignition:** either the oxidizer or fuel to be in a liquid or vapor state to allow interaction
- Many oxidizers are ionic solids (KNO₃), and the “looseness” of the lattice is important in determining reactivity:
  - Increased temperature, the vibrational motion of the lattice increases
  - Liquid fuel components can more easily diffuse into the lattice, even if the oxidizer is still solid, and begin to interact below the melting or decomposition temperature

**Audience Survey Question**

**Tammann Temperature is significant because?**

- It is approximately two times the melting point in kelvin
- It is temperature at which the mobility and reactivity of the molecules in a liquid state become appreciable
- It has 70% of the vibrational freedom present at the melting point and can cause ignition in a reaction
- It is ideal temperature for ignition of any material
Tammann Temperature

- Prof G. Tammann proposed that this diffusion is significant at “halfway” to the melting point (the “Tammann temperature”) and has 70% of the vibrational freedom present at the melting point → often sufficient for reaction leading to ignition
- KNO$_3$ melts at 334 °C (607 K), but the Tammann temperature is 30.5 °C (303.5 K), just a hot day in August!

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Formula</th>
<th>Melting point, °C</th>
<th>Melting point, K</th>
<th>Tammann temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium nitrate</td>
<td>NaNO$_3$</td>
<td>307</td>
<td>580</td>
<td>17</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>KNO$_3$</td>
<td>334</td>
<td>607</td>
<td>31</td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KClO$_3$</td>
<td>356</td>
<td>629</td>
<td>42</td>
</tr>
<tr>
<td>Strontium nitrate</td>
<td>Sr(NO$_3$)$_2$</td>
<td>570</td>
<td>843</td>
<td>149</td>
</tr>
<tr>
<td>Barium nitrate</td>
<td>Ba(NO$_3$)$_2$</td>
<td>592</td>
<td>865</td>
<td>160</td>
</tr>
<tr>
<td>Potassium perchlorate</td>
<td>KClO$_4$</td>
<td>610</td>
<td>883</td>
<td>168</td>
</tr>
<tr>
<td>Lead chromate</td>
<td>PbCrO$_4$</td>
<td>844</td>
<td>1117</td>
<td>286</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>Fe$_2$O$_3$</td>
<td>1565</td>
<td>1838</td>
<td>646</td>
</tr>
<tr>
<td>Magnesium metal</td>
<td>Mg</td>
<td>651</td>
<td>924</td>
<td>189</td>
</tr>
</tbody>
</table>

Sensitivity Analysis

- An energetic material must be sensitive to ignition if it is to be of any use
- But the safe handling and storage of the material must be of highest importance
- Understanding a material’s sensitivity is extremely important for storage and use, and therefore full sensitivity testing should be run on any new composition as a standard matter of course

- Thermal sensitivity
- Electrical/spark sensitivity (including static electricity)
- Impact sensitivity
- Friction sensitivity
Ignition Sensitivity Curve

A specified level of energy is applied – does ignition occur?  
→ Ignition is a statistical event, therefore sensitivity is statistical

**Audience Survey Question**

ANSWER THE QUESTION ON BLUE SCREEN IN ONE MOMENT

Which of the following are viable Pyrotechnic Sensitivity Tests?

- Impact, sample, static, reference, and shock
- Zap, pow, boom, kapow, and bam
- Friction, thermal, booster, acceptor, and shock
- Impact, friction, electrostatic, thermal, and shock
- Audio, visual, scratch & sniff, tactile, and tongue
Types of Sensitivity Tests

Thermal Sensitivity

- At what temperature does the system ignite?
- Probably the best understood of all phenomenon
- Measured through DTA, DSC, time-to-ignition studies

Nitrocellulose – DSC and Time-To-Ignition Study
Spark Sensitivity

- Usually measured with a needle electrode (cathode) that approaches a sample sitting on a grounded surface (anode).
- The energy of the spark is controlled by varying capacitance and voltage and is measured in Joules: \( J = \frac{1}{2} CV^2 \).
- Humans generate \( \sim 15-20 \text{ mJ} \) (0.020 J) of energy, enough to ignite some compositions and many organic solvents (acetone, ethyl ether, methanol, etc).
- Conductive materials (metals) tend to increase the spark sensitivity of compositions.
- Adding non-conductive materials (diatomaceous clay) can reduce the spark sensitivity (but also adversely affect the performance).

Spark Sensitivities

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ignition Energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RDX</td>
<td>&gt; 4.5</td>
</tr>
<tr>
<td>Mg/NaNO₃/binder 55/40/5</td>
<td>&gt; 4.5</td>
</tr>
<tr>
<td>Si/KNO₃ 50/50</td>
<td>&gt; 0.45 &lt; 4.5</td>
</tr>
<tr>
<td>Al/KClO₄ 22.5/77.5</td>
<td>&gt; 0.04 &lt; 0.45</td>
</tr>
<tr>
<td>Mg/BaO₂/Binder 12/86/2</td>
<td>&gt; 0.001 &lt; 0.045</td>
</tr>
<tr>
<td>B/MoO₃ 25/75</td>
<td>0.00025</td>
</tr>
</tbody>
</table>

Source: J.M. Jenkins (UK); Lecture Notes (1980)
Static Electricity

- Every effort should be made to eliminate static electricity from the manufacturing and storage processes!

Friction Sensitivity

- A very important test, as many chances for friction to occur appear in production: mixing, pouring, pressing – generation of hot spots or interaction of materials at a chemical level
- Grittiness of the material can increase sensitivity (sometimes desired, sometimes not)
- Rotary friction – yields numerical value
- Sliding surface – yields a fire/no-fire result at a specific force
### Rotary Friction Sensitivities

<table>
<thead>
<tr>
<th>Composition</th>
<th>Ignition Energy (ft-lb²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>IM 28 Incendiary</strong></td>
<td>19</td>
</tr>
<tr>
<td>Barium Nitrate 40</td>
<td></td>
</tr>
<tr>
<td>Potassium Perchlorate 10</td>
<td></td>
</tr>
<tr>
<td>Mg/Al Alloy 50</td>
<td></td>
</tr>
<tr>
<td><strong>SW522 Smoke</strong></td>
<td>52</td>
</tr>
<tr>
<td>Potassium Perchlorate 20</td>
<td></td>
</tr>
<tr>
<td>Potassium Nitrate 20</td>
<td></td>
</tr>
<tr>
<td>Aluminum 20</td>
<td></td>
</tr>
<tr>
<td>Zinc Dust 40</td>
<td></td>
</tr>
<tr>
<td><strong>M22 Flash Mixture</strong></td>
<td>74,357</td>
</tr>
<tr>
<td>Magnesium (200/325) 75</td>
<td></td>
</tr>
<tr>
<td>Teflon 10</td>
<td></td>
</tr>
<tr>
<td>Viton 15</td>
<td></td>
</tr>
</tbody>
</table>

*Source: Aikman, et al; PEP 12, p.17 (1987).*

---

### Impact Sensitivity

- The DOT and DoD use the Bureau of Explosives (BoE) impact machine to determine impact sensitivity.
- A specified weight is dropped from a specified height a specified number of times.
- Cannot re-use a non-ignited sample (pressed).
- Usually reported in 10% or 50% ignition values, or minimum observed.
- Generation of “hot spots” in the material.
Impact vs. Friction Sensitivity

<table>
<thead>
<tr>
<th>% Comp. Zr/KClO₄</th>
<th>Impact Sens. Height of 50% Explosion (cm)</th>
<th>Friction Sens. Pistil Load upto which Insensitive (Kgf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/90</td>
<td>115</td>
<td>36.0</td>
</tr>
<tr>
<td>20/80</td>
<td>106.5</td>
<td>36.0</td>
</tr>
<tr>
<td>30/70</td>
<td>106.25</td>
<td>36.0</td>
</tr>
<tr>
<td>40/60</td>
<td>90.0</td>
<td>14.4</td>
</tr>
<tr>
<td>50/50</td>
<td>92.5</td>
<td>10.8</td>
</tr>
<tr>
<td>60/40</td>
<td>99.1</td>
<td>5.4</td>
</tr>
<tr>
<td>70/30</td>
<td>92.5</td>
<td>4.8</td>
</tr>
<tr>
<td>80/20</td>
<td>103.0</td>
<td>3.6</td>
</tr>
<tr>
<td>90/10</td>
<td>94.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Factors Affecting Sensitivity

- Homogeneity
- Particle morphology and size
- Grain size of blended material
- Residual moisture or organic solvent
- Formula and percent composition
- Presence of grit, foreign material, acids, bases
- Chemical incompatibility (acids, moisture, etc)

- Changes to ANY ONE of these will affect sensitivity
- Be warned of static electricity!
Instrumental Analysis

- Modern instruments and methods have provided pyrotechnicians with substantial new abilities and a wealth of information.

**Ability to Study and Analyze:**
- Chemical makeup and purity
- Ignition processes
- Sensitivity to ignition
- Micro-structure of solids and mixture layouts
- Thermal/barometric behavior and output
- Reaction products
- Quantification of visual and auditory effects
- Effects of external stimuli (environment, time) on compositions
Some Instrumentation and Techniques

- Differential Thermal Analyzer (DTA)
- Differential Scanning Calorimeter (DSC)
- Spark Sensitivity Device
- Impact/Shock Sensitivity Device
- Friction Sensitivity Device
- Microscopy
- Particle Size Analyzer
- Fourier-Transform Infrared Spectrometer (FTIR)
- Ultraviolet-Visible Spectrometer (UV-Vis)
- Thermogravimetric Analyzer
- X-Ray Crystallography
- X-Ray Diffraction
- Gas chromatography
- Atomic Emission Spectroscopy
- Optical Emission Spectroscopy
- Raman Spectroscopy
- Nuclear Magnetic Resonance (NMR)
- X-Ray Fluorescence Spectroscopy
- Moisture analysis
- Calorimeter
- Barometer
- Voltameter
- Liquid Chromatography
- Mass Spectrometry
- Atomic Absorption Spectroscopy
- Flame Ionization Detector
- Footcandle Light Meter
- Volume Unit Meter
- Densitometer
- Ion-Mobility Spectrometry
- Neutron Diffraction Crystallography
- Pyrolysis Effluent Gas Detection (EGD)
- Melting point apparatus

Emission Spectroscopy Uses

- Quantifying color output of colored compositions
- But remember: the human eye is not an electronic spectrometer, it is much more complicated!
- What looks like a fantastic green on the computer may be “rather meh…” to the human eye, or vice-versa.

- Optical Emission Spectroscopy (OES) - determination of purity of compounds, including identification of impurities with quantification
  - Extra sodium causing too much yellow to overpower, too much strontium in the barium compound, etc.
Red Flare Emission Spectrum

Green Flare Emission Spectrum
Microscopy

- “Looking small”
- Using microscopes to enhance visualization material that may not be visible with the naked eye
- Optical - standard magnifying glass/microscope
- Electron – using a beam of electrons to illuminate the specimen
  - TEM – transmission electron microscope (older) – maps the resulting diffracted electrons to form the image
  - SEM – scanning electron microscope (modern) – analyzes resulting emissions to determine map of the target
- Scanning – using a physical probe to scan the surface
  - STM – scanning tunneling microscopy
  - ATM – atomic force microscopy

KNO₃ under a Microscope
SEM Of Thermite - Al/Fe$_2$O$_3$

Optical/SEM of Activated Charcoal
Thermoanalysis

- Study of the thermal properties of compositions is exceedingly valuable to the pyrotechnician:
  - Ignition temperature/time-to-ignition
  - Burning temperature
  - Calorimetry
  - Differential Thermal Analysis (DTA)
  - Differential Scanning Calorimetry (DSC)
  - Thermal Gravimetry (TG)
  - Evolved Gas Analysis (EGA)
  - Pyrolysis – Analysis of effluent gas
Ignition Temperature

- Measured temperature of ignition of a composition
- Decomposition or activation of materials to allow interaction
  - Release of oxygen/oxidizer
  - Fuel in a state to be oxidized

- Rate of heat release must be sufficient to sustain further burning
- Measured by direct heat application (when did it burn?), DTA, or DSC

DTA

- Differential Thermal Analysis – measures the difference in temperature between an analyte and reference sample (that just gets hot at a steady rate)
- Endotherm – analyte not increasing in temperature with reference
- Exotherm – analyte hotter than reference
Thermogram of Potassium Nitrate

- 130 °C – rhombic to trigonal crystalline transition (requires energy/heat)
- 334 °C - melting

Thermogram of Sulfur

- 105 °C – rhombic to monoclinic crystalline change
- 119 °C – melting
- 180 °C – fragmentation of liquid S8 into smaller units
- 450 °C – vaporization
Thermogram of Black Powder

105/119 °C – Solid phase transition and melting of sulfur (overlap)
130 °C – rhombic to trigonal crystalline transition
334 °C – potassium nitrate melting, followed by exotherm (ignition)
→ Release of oxygens from KN major player in ignition

Conclusion: Analyzing your Composition

- Microscopy
- Suite of sensitivity tests
- Thermal analysis / ignition temperatures
- Functional analysis (did it work?)
- Analysis of desired output:
  - Color – spectroscopy
  - Light/Obscuration – photometry/light meter
  - Gas generation – TGA/gas analyzer
  - Sound – sound level meter/loudness meter
- Chemical analysis/Forensics – Chromatography/mass spec, IR, UV-Vis, Raman, x-ray fluorescence, x-ray diffraction, &c
Safety!

- All pyrotechnic compositions are sensitive to some form of stimulus: heat/flame, spark, shot, friction, shock
- Every effort needs to be made to handle materials safely
- Do not experiment with chemicals that you do not understand!

Other Resources

- A.A. Shidlovskiy, *Principles of Pyrotechnics*
- J.A. Conkling, C.J. Mocella, *Chemistry of Pyrotechnics*
- Journal of Pyrotechnics, Pyrotechnic Chemistry
- American Pyrotechnics Association
- Pyrotechnics Guild International
- Local hobbyist clubs
What is your favorite memory of a fireworks show?

• Independence Day (U.S.)
• Bonfire Night/Guy Fawkes Night (U.K)
• Setting off snappers and bottle rockets as a kid
• New Year / Chinese New Year
• [Can’t tell you, we bent some laws doing it, but it was AWESOME!]

Thanks For Attending!
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