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ACS WEBINARS™
December 8, 2011

Welcoming 2012: The Chemistry of Fireworks

Andrew Maynard
University of Michigan

Chris Mocella
Summer Pyrotechnic Seminars

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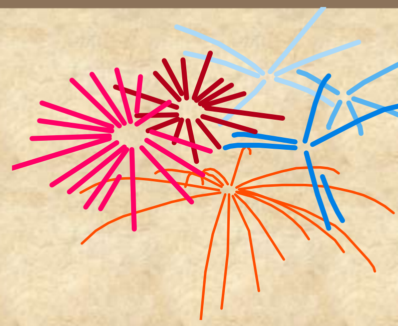
The Chemistry of Fireworks



Chris Mocella

(with many thanks to Dr. John Conkling)

ACS Webinar

December 8, 2011

The "Chem 101" of Fireworks:

- Redox Reactions
- Thermochemistry
- Stoichiometry
- States of matter
- Emission spectroscopy
- Surface chemistry

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Basics of Pyrotechnics/Fireworks

1. Oxygen source (oxidizer)
   + electron source (fuel)
   → Products + Energy
2. Energy Output =
   Light, Color, Sound, Pressure,
   Motion, &c. The “effect”

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Electron Transfer - Redox

- $3KClO_4 + 8Al \rightarrow 3\ KCl + 4\ Al_2O_3$
  - Oxidizer - potassium perchlorate
  - Fuel - aluminum metal
  - 3(138.5):8(27) = 66:34 parts by wt. for stoichiometric oxygen balance
  - The aluminum is oxidized and the chlorine is reduced
  - This is a classic “flash powder” formulation

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Heat Output Factors

- 1. Selection of chemicals - oxidizer and fuel can make a formulation more or less energetic based on reaction temperatures /heats of reaction
- 2. Weight ratio of chemicals: a stoichiometric mix should produce the maximum heat in kcal or kJ per gram of mix, assuming all oxygen comes from the oxidizer.
- Other factors such as heat conductivity (metals) and "pre-heating" can have a dramatic effect in speeding up total reaction time.

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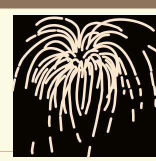
Ingredients for Pyrotechnic Mixtures



- 1. Oxidizing agents (oxygen-rich, occasionally fluorine is used)
- 2. Fuels (organic, metallic, other)
- 3. Color ingredient
- 4. Intensifier
- 5. Binder (small %) – can also act as a fuel

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Oxidizers (oxygen donors)

- These chemicals release oxygen atoms when heated to elevated temperatures; this oxygen reacts with a fuel to produce energy/heat.
- *Potassium nitrate*, KNO_3, saltpeter
- *Potassium perchlorate*, $KClO_4$
- *Strontium nitrate*, $Sr(NO_3)_2$ (red flame color)
- *Barium nitrate*, $Ba(NO_3)_2$ (green flame color)
- *Ammonium perchlorate*, NH_4ClO_4
- *Teflon*, $(C_2F_4)_n$ (fluorine as the oxidizer)

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Oxidizers and their Reactions

- $2\ KNO_3 \rightarrow K_2O + N_2 + 5$ O's
- $KClO_4 \rightarrow KCl + 4$ O's
- N goes from +5 to 0 (gains 5 e's)
- Cl goes from +7 to -1(gains 8 e's)

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Considerations for Oxidizers

- Low hygroscopicity (keep your powder dry!)
- Proper flame color
- Readily decomposes to produce oxygen (minimal energy cost)
- High % of active oxygen
- Stable (does not readily decompose in storage)
- “Green” chemistry – try to keep out perchlorates or other toxic chemicals

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Fuels

These chemicals are oxidized, or “burned” by the oxygen released by the oxidizer, producing heat.

- Metal Powders (high heat output): Al, Mg, Mg/Al alloy (“magnalium”), Fe, Ti
- Elemental Fuels: C(charcoal), S, P(watch out!)
- Carbon/hydrogen “Organic” Compounds: starches, sugars, plastics (PVC), tree gums and resins,

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Ignition

- Reach a temperature where the oxidizer is releasing oxygen at a fast rate and fuel is activated to be able to accept the oxygen to produce oxidized products – heat that is then released, propagating the reaction

→Light a small portion, and the rest goes “poof”

- Possible ignition sources – flame, friction, impact, spark, elevated temperature, chemical incompatibility (actually, too much compatibility!)

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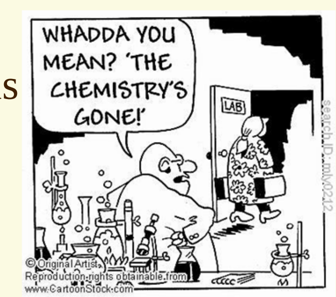
Other factors

Chemistry alone doesn’t govern fireworks!

- Extent of mixing
- Purity of starting chemicals
- Particle sizes
- Degree of confinement
- Effect of water
- Form – powder, pellet, pressed into a tube



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Poll:

Black powder, or gun powder, is one of the oldest firework formulations:

How long do you think the current formulation/recipe for black powder has been in use?

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The original firework: Black Powder

First thought to have been used in ca 1000 A.D., the same formulation has been used since ca. 1500 A.D. Is there any other technical recipe that you can think of that has lasted five hundred years?

BLACK POWDER

Potassium nitrate, KNO_3	75 pts. by wt.
Charcoal, C	15 pts. by wt.
Sulfur, S	10 pts. by wt.

Performance varies dramatically by the extent of mixing, how it was mixed (wet/dry, pressing), purity of starting materials (potassium nitrate is hygroscopic, different forms of charcoal).

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Black powder – fascinating!

- 75:15:10 ratio by weight – 500+ years old
- The first “energetic material” has been used as an explosive, propellant, and pyrotechnic material, even today
- Illustrates the “culinary art” of fireworks – follow the recipe exactly, but preparation and presentation are everything!

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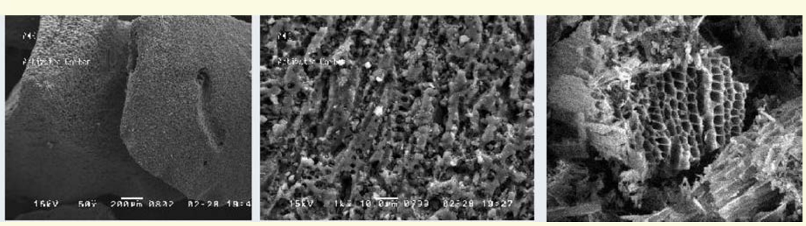
Effects of Charcoal

- Intimate mixing and coating of charcoal’s “pores” with sulfur and potassium nitrate can dramatically affect the output:



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Pyrotechnics Used in Fireworks

- Fuse / Delay
- Propellant, “lift charge”
- Burst charge
- “Report” – a concussion/sound
- Color/light (stars, sparks, strobe, crackle)
- Whistle
- Smoke – sometimes wanted, sometimes not



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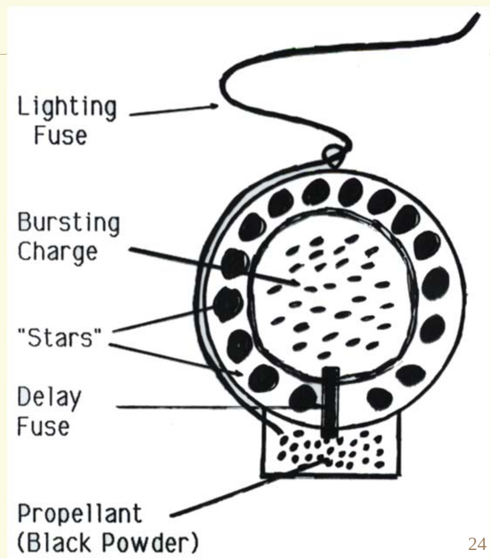
Chrysanthemum Shell (Japan, China)



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Light Processes

1. Atomic Emission (vapor)
2. Molecular Emission (vapor)
3. Black Body Emission (solid/liquid)

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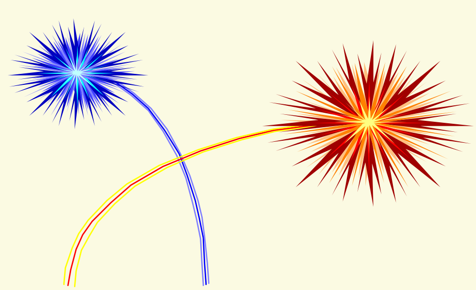
Heats of Reaction - high heat output enhances light output

$KClO_4$/Mg (60/40)	2.24 kcal/g
$NaNO_3$/Mg/polyester (44/50/6)	2.0
Black Powder (KNO_3/S/C)	0.66



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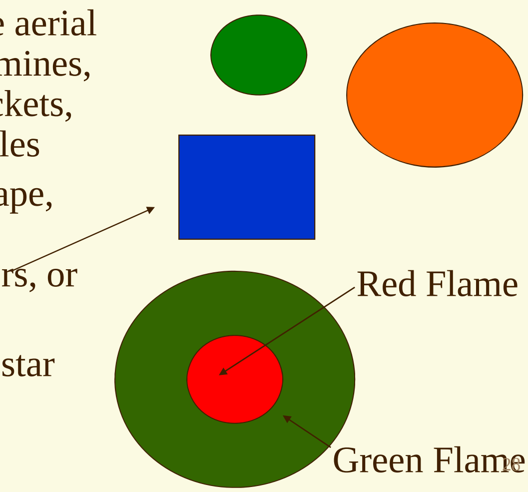
Colors

- Red - strontium compounds
- Orange – calcium compounds
- Blue - copper compounds
- Green - barium or boron compounds
- Yellow - sodium atoms
- Violet - strontium and copper
- White - aluminum or titanium metal (hot burn)

“Stars”

- Used to produce aerial color effects in mines, aerial shells, rockets, and roman candles
- Vary in size, shape, and burn rate - spheres, cylinders, or cubes
- Color changing star



Colors and Mixing

- Various colors (wavelengths of visible light) can be mixed to produce other colors.
- Examples:
  – red and blue produce violet
  – green and orange produce yellow
- However, too many emitters produce a "washed out" white visible effect

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Blue Fireworks

- Blue is one of the most difficult colors to produce in fireworks
- Radical vapor-state CuCl• is an excellent blue emitter, but decomposes at relatively low temperatures (can't burn too hot/bright)
- Many "red, white, and blue" fireworks are often red-white-and-purple" to allow the audience to see the color with added (brighter) strontium compounds

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A Magnalium Red Formulation

Potassium Perchlorate	55
Strontium Carbonate	15
Parlon (chlorinated rubber)	15
Red Gum (fuel, binder)	9
Magnalium (50/50, -200 mesh) (alloy of Mg and Al – hot fuel)	6

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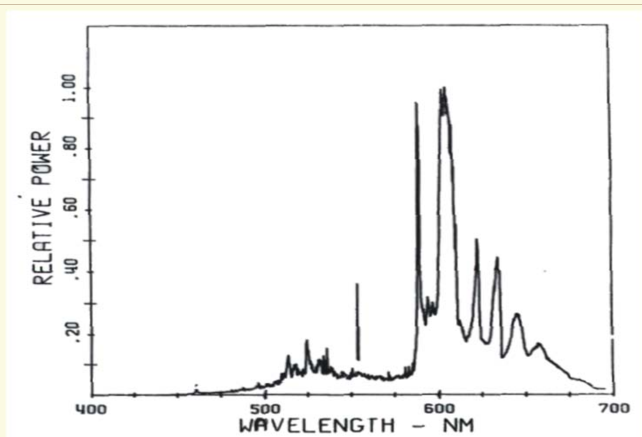
MK 124 Red Flare Emission Spectrum



But remember: the human eye is not a digital spectrophotometer! What matters is what looks good to us.

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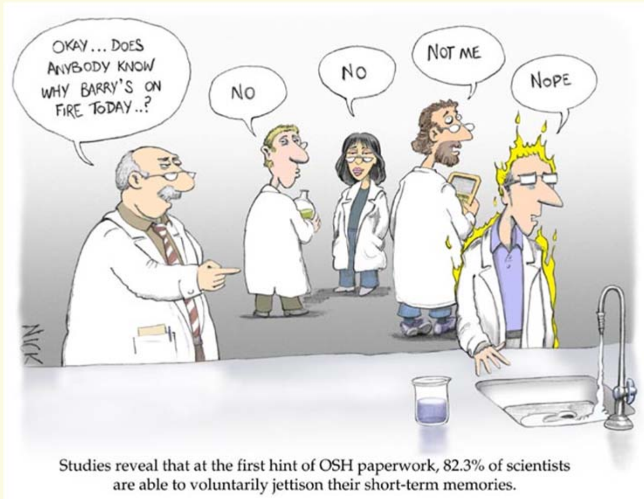
Remember: Be Safe!



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Other Resources:

- A.A. Shidlovskiy, *Principles of Pyrotechnics*
- T. Shimizu, *Fireworks, The Art, Science, and Technique*
- J.A. Conkling, C.J. Mocella, *Chemistry of Pyrotechnics*
- Journal of Pyrotechnics, Pyrotechnic Chemistry
- American Pyrotechnics Association
- Local hobbyist clubs and groups

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Thanks for attending!

("oooh… ahhh…. vapor-state copper chloride emitters…") 35

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Thursday, December 15, 2011

Chemicals and the Economy – Year-End Review & 2012 Projections

Paul Hodges, International eChem
Bill Carroll, Occidental Chemical Corporation

Thursday, January 12, 2012

New Year and New Patent Laws Scientists Should Know

Michael Brodowski, partner of K&L Gates LLP

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