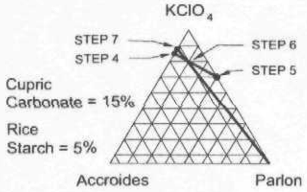

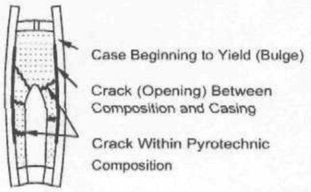

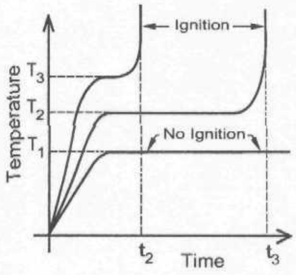

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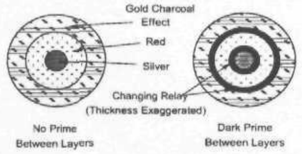

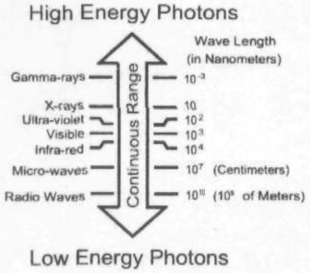

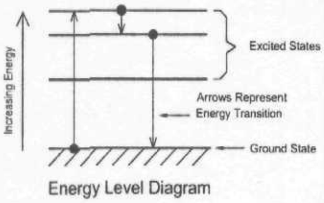

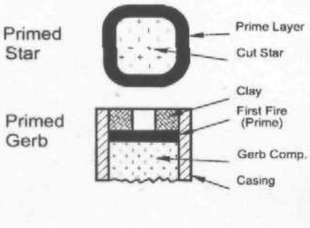

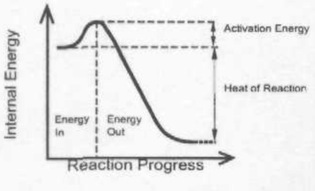

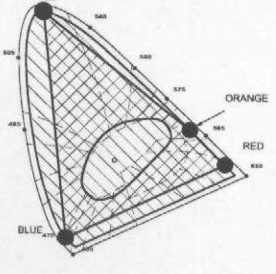

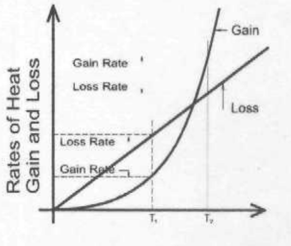

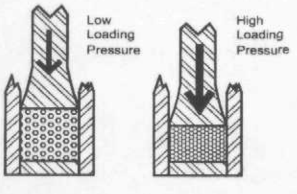

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CAUTION

The experimentation with, and the use of, pyrotechnic materials can be dangerous; it is important for the reader to be duly cautioned. Anyone without the required training and experience should never experiment with nor use pyrotechnic materials. Also, the amount of information presented in these lecture notes is not a substitute for the necessary training and experience.

A major effort has been undertaken to review this text for correctness. However, it is possible that errors remain. Further, it must be acknowledged that there are many areas of pyrotechnics, fireworks in particular, for which there is much "common knowledge", but for which there has been little or no documented research. For the sake of completeness, these lecture notes certainly contain some of this unproven common knowledge. It is the responsibility of the reader to verify any information herein before applying that information in situations where death, injury, or property damage could result.

Course Outline

1 Basic Chemical Principles

- Atomic Structure and Periodicity
- Chemical Bonds and Bond Types
- Chemical Names
- Chemical Formulas, Equations and Stoichiometry
- Common Pyrotechnic Materials

2 Pyrotechnic Chemistry, Ignition and Propagation

- Oxidation States and Oxidation Numbers
- Oxidation–Reduction Reactions
- Pyrotechnic Compositions
- Pyrotechnic Reaction Energy Considerations
- Pyrotechnic Ignition
- Pyrotechnic Propagation

3 Pyrotechnic Primes and Priming

- Pyrotechnic Primes
- Shimizu Energy Diagrams
- Ignition and Propagation Problems
- Prime Formulations
- Priming Techniques
- Alternatives to Priming

4 Factors Affecting Burn Rate

- Choice of Fuel / Oxidizer and Ratio
- Degree of Mixing
- Particle Size and Shape
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- Temperature, Pressure and Confinement
- Physical Form and Consolidation
- Geometry, Crystal and Environmental Effects

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- Parallel vs. Propagative Burning
- Black Match / Quick Match Mechanism
- Rocket Performance / Malfunctions
- *Burning / Deflagration / Detonation*

6 Physical Basis for Colored Light Production

- Nature of Light
- Basic Quantum Theory
- Line, Band and Continuous Spectra
- Chromaticity Diagram
- Classical Color Theory
- Color Theory Applied

7 Chemistry of Colored Flame

- Mechanism of Colored Light Production
- Color Agents and Color Species
- Basic Red Color Chemistry
- Optimizing Color Quality
- Green, Orange, Blue, Yellow and Purple
- Other Topics

8 Chemistry of Sparks, Glitter and Strobe

- Sparks and Incandescent Light Emission
- Control of Spark Duration
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9 Pyrotechnic Smoke and Noise

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- Chemical Smoke
- Whistles
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10 Approaches to Formulation Development

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- Stoichiometric Approach
- Other Approaches

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- Water Reactivity
- Auto-Ignition Temperature
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- Impact Sensitiveness
- Electrostatic Sensitiveness
- Cautions about Sensitiveness Indicators

12 Pyrotechnic Hazard Management

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- Pyrotechnic Hazards
- Hazardous Chemical Combinations
- Control of Hazards

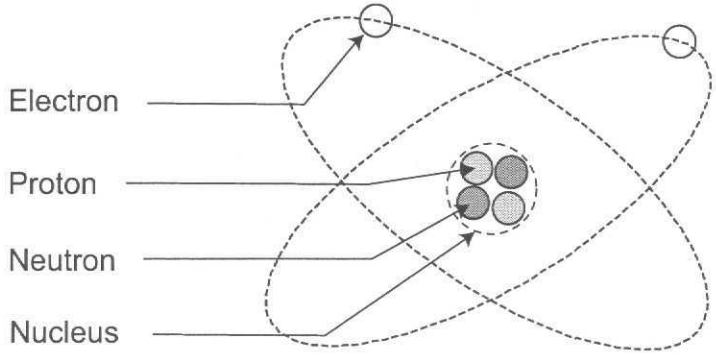
SECTION 1

BASIC CHEMICAL PRINCIPLES

- Atomic Structure and Periodicity
- Chemical Bonds and Bond Types
- Chemical Names
- Chemical Formulas, Equations, and Stoichiometry
- Common Pyrotechnic Materials

ELEMENTARY ATOMIC PARTICLES

- An atom is the smallest unit of matter that maintains its chemical identity and characteristics.
- Atoms are composed of 3 types of smaller entities. These subatomic particles are electrons, protons and neutrons.



Particle Type	Relative Mass	Relative Volume Occupied	Particle Charge	Number in Atom
Proton	≈2000	1	+1	N_p
Neutron	≈2000	1	0	$N_p \leq N_n < 2N_p$
Electron	1	≈1,000,000,000,000	–1	$N_e = N_p$

CHEMICAL ELEMENTS

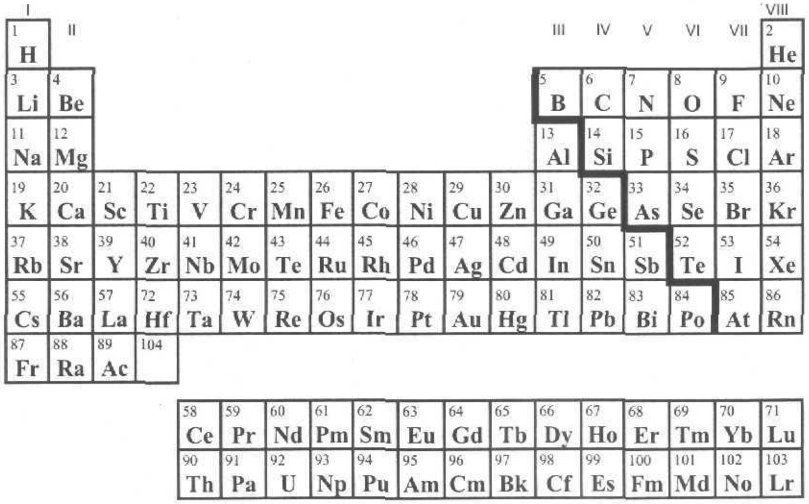
- **There are more than 100 different chemical elements, each of which is characterized by the number of protons in the nucleus (atomic number). They each have a unique atomic symbol.**

Element	Atomic Number	Atomic Symbol
Hydrogen	1	H
Helium	2	He
Lithium	3	Li
Beryllium	4	Be
⋮	⋮	⋮
Fluorine	9	F
Neon	10	Ne
Sodium	11	Na
Magnesium	12	Mg
⋮	⋮	⋮
Argon	18	Ar
Potassium	19	K
⋮	⋮	⋮

- **When chemical elements are listed in order of atomic numbers, *it is observed that their chemical and* physical properties repeat periodically (e.g., He, Ne, and Ar are all similar; as are Li, Na, and K).**

PERIODIC TABLE

- **When the chemical elements are presented as a table in which elements with similar chemical and physical properties appear in vertical columns, the result is the "Periodic Table of Elements".**



I	II											III	IV	V	VI	VII	VIII
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Te	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104														
				58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
				90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- **In the table, group VIII elements (Helium, Neon, Argon, etc.) are all non-reactive gases, and group I elements (beginning with Lithium) are all highly reactive, are ductile metals, and react 1:1 with group VII elements.**

- **Heavy line divides metals on left from non-metals on right.**

MAGIC NUMBERS AND ELECTRON SHELLS

- The pattern of outermost atomic electrons repeats after certain specific atomic numbers:

2 10 18 ...

(so-called magic numbers)

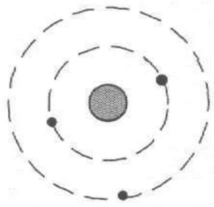
- Repeating outer electron structures are the result of electrons residing in shells around the nucleus.
- There is a maximum number of electrons allowed in each shell. This gives rise to the magic numbers.

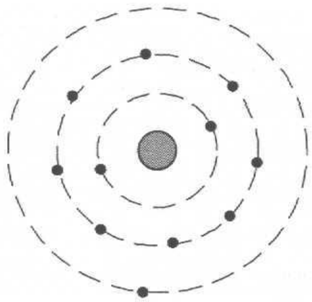
Shell Number	1	2	3	...
Max. Electrons per Shell	2	8	8	...
Magic Numbers	2	10	18	...

- The above explanation is simplistic but sufficient for the purpose of this course.

CHEMICAL PERIODICITY

- Generally, chemical bonding only involves outer electrons. Accordingly, when the outer electron structure repeats, so do chemical bonding tendencies. In turn, this means that chemical and physical properties also tend to repeat.





Lithium has 3 electrons

- 2 in first shell
- 1 in outer shell

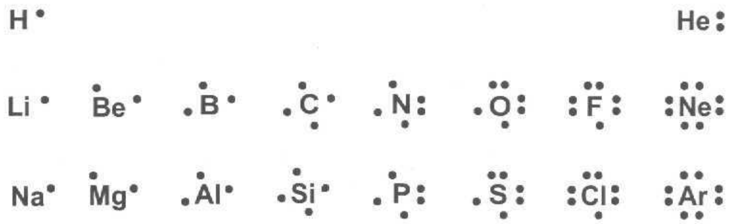
Sodium has 11 electrons

- 2 in first shell
- 8 in second shell
- 1 in outer shell

- The presence of only one electron in the outer shell is why lithium and sodium are similar in their chemistry.

ELECTRON DOT (LEWIS) STRUCTURES

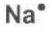
- Only the electrons in outer shells are shown; these are the electrons principally involved in chemical bond formation. (For example, hydrogen, lithium and sodium are each shown with only one dot, because they each have a single outer electron.)



- Atoms combine (form bonds) to achieve greater stability, in a way that combines overall electrical neutrality with filled electron shells. They do this in one of two ways:
    - By transferring electrons between the atoms. This results in an "ionic" bond.
    - By sharing electrons between the atoms. This results in a "covalent" bond.
- Pyrotechnists care about chemical bonds because that is the way pyrotechnic energy is produced.

IONIC CHEMICAL BONDS

- Ionic Bonds — Chemical bonds between atoms that achieve full shell electron configurations by TRANSFERRING electrons, and in the process become charged ions.

Atom	Atomic Number	Electron Configuration	Nearest Magic No.	Desired Change
Na	11		10	Lose 1 electron
Cl	17		18	Gain 1 electron
Mg	12		10	Lose 2 electrons
F	9		10	Gain 1 electron
Li	3		2	Lose 1 electron

- Examples:

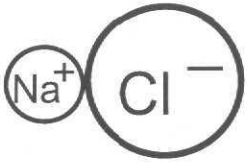
(NaCl)

(MgF_2)

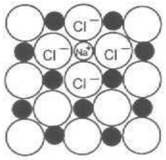
(Electrical neutrality is achieved by the ions clustering together to balance their charges.)

STRUCTURE OF IONICALLY BOUND CHEMICALS

- These chemical compounds consist of positive and negative "ions" (electrically charged atoms), which are held together by electrostatic forces.



- Ions with the same charge repel each other; oppositely charged ions attract each other. Thus, as solids, the ions arrange themselves in highly ordered patterns (crystals) such as:



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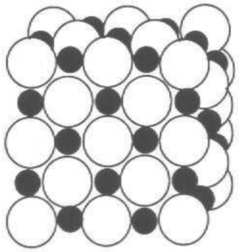


3-Dimensional Pattern

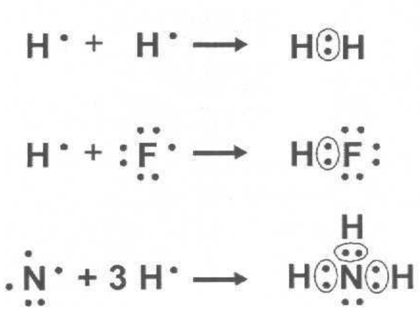
- Many ionically bound compounds are in the general category called "salts".

COVALENT CHEMICAL BONDS

- Covalent Bonds — Bonds between atoms that achieve full-shell electron configurations by <u>SHARING</u> electrons.

Atom	Atomic Number	Electron Configuration	Nearest Magic No.	Desired Change
H	1	$H\cdot$	2	Share 1 electron
F	9	$:\ddot{\underset{\cdot}{F}}:$	10	Share 1 electron
O	8	$\cdot\ddot{\underset{\cdot}{O}}:$	10	Share 2 electrons
N	7	$\cdot\dot{\underset{\cdot}{N}}:$	10	Share 3 electrons

- Examples:



$$H\cdot + H\cdot \longrightarrow H{:}H$$

Hydrogen molecule

$$H\cdot + :\ddot{\underset{\cdot\cdot}{F}}\cdot \longrightarrow H{:}\ddot{\underset{\cdot\cdot}{F}}:$$

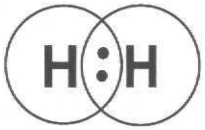
Hydrogen fluoride

$$\cdot\dot{\underset{\cdot\cdot}{N}}\cdot + 3\,H\cdot \longrightarrow H{:}\overset{\overset{H}{\cdot\cdot}}{\underset{\cdot\cdot}{N}}{:}H$$

Ammonia

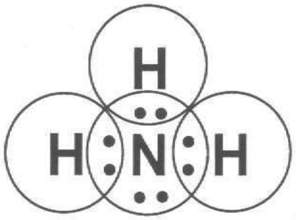
STRUCTURE OF COVALENTLY BONDED CHEMICALS

- These materials consist of relatively small groups of atoms (molecules) held together as a consequence of lowered energy, which results from sharing electron pairs.



H_2

Hydrogen molecule



NH_3

Ammonia molecule

- The shape of molecules is mostly a consequence of the number and type of electron pairs shared.
- The atoms within a molecule are fairly tightly bound, but often there is relatively little attraction between the individual molecules themselves; this produces relatively low melting and boiling points as compared with ionically bonded chemicals.

ELECTRON TRANSFER VS. ELECTRON SHARING

- Chemical bond type (i.e., whether there is electron transfer or electron sharing) is determined by the relative affinity of atoms for the electrons forming the bond.

Large Affinity Difference → Electron Transfer → Ionic Bond

Examples of ionic bonds:

NaCl — Sodium chloride
MgF_2 — Magnesium fluoride
MgO — Magnesium oxide

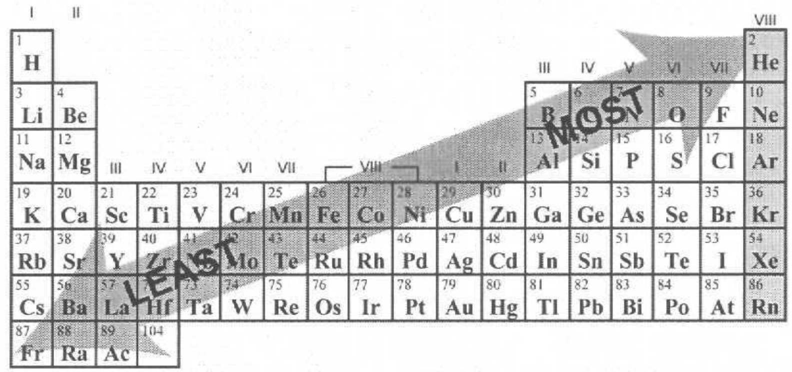
Small Affinity Difference → Electron Sharing → Covalent Bond

Examples of covalent bonds:

H_2 — Hydrogen molecule
NH_3 — Ammonia
CH_4 — Methane

ELECTRONEGATIVITY

- Electronegativity is a measure of an atom's affinity for electrons.



- Atoms like F, Cl and O demonstrate a great affinity for electrons. Acquiring one or two electrons completes their outer electron shells.

- Atoms like Na, K and Mg demonstrate a low affinity for electrons. The loss of one or two electrons depletes their outer electron shell resulting in their next lower (completely full) electron shell being their outermost shell.

- Group VIII atoms have a full outer shell and effectively zero electron affinity.

ELECTRONEGATIVITY DIFFERENCE AND CHEMICAL BOND TYPE

- Electronegativities range from approximately 1 to 4.

- Examples of electronegativity differences and the types of chemical bonds resulting.

Molecule	Electronegativity Difference		Bond Type
KCl	2.34	large	Ionic
MgO	2.13		Ionic
LiF	3.00		Ionic
H_2	0.00	small	Covalent
NO_2	0.40		Covalent
CH_4	0.35		Covalent
ZnS	0.93	med.	Polar Covalent
H_2O	1.24		Polar Covalent

- A polar covalent bond is a chemical bond in which there is an unequal sharing of electrons.

ENERGY CONSIDERATIONS REGARDING CHEMICAL BONDS

- Atoms combine (form bonds) to achieve greater stability, in a way that combines electrical neutrality with full-shell electron configurations. When chemical bonds form, energy is produced.

- For example, each separate hydrogen atom has electrical neutrality but not in its full-shell configuration. When they combine to form a hydrogen molecule, they accomplish both.

$$H + H \rightarrow H_2 + \text{energy} \quad (218\ \text{kJ/g})$$

Similarly:

$$2\,H + O \rightarrow H_2O + \text{energy} \quad (258\ \text{kJ/g})$$

$$Zn + S \rightarrow ZnS + \text{energy} \quad (8\ \text{kJ/g})$$

- In order to break chemical bonds, the energy released upon bond formation must be replaced.

$$H_2 + \text{energy}\ (218\ \text{kJ/g}) \rightarrow 2\,H$$

STATES OF MATTER

- The common states of matter are solids, liquids and gases.

- Solids:
    - Atoms (or molecules) packed tightly together in a rigid structure.
    - Both volume and shape are constant.

- Liquids:
    - Atoms (or molecules) clump together loosely in temporary clusters.
    - Volume is constant but shape is not.

- Gases:
    - Atoms (or molecules) move independently and freely until they collide with one another or a wall of a container.
    - Neither volume nor shape is constant.

ROLE OF TEMPERATURE IN STATES OF MATTER

- **Temperature is an indication of the amount of energy associated with the random motion of atoms or molecules.**

  High Temperature → Much Motion Energy

- **At absolute zero temperature (0 K, –273 °C, –460 °F), all matter is solid and vibrational motion is at an absolute minimum.**

- **As temperature rises, vibrational energy increases. At some point the vibrational motions become so great that the rigid structure of solids breaks down (i.e., they melt to become liquid).**

- **As temperature continues to rise, a point is reached where even the loose grouping of liquids also breaks down and gases are produced (i.e., they vaporize).**

- **The temperature at which these changes of state take place depends in part on how tightly the atoms or molecules are bound together.**

Strong Ionic Bonds → High melting and boiling points

Strong Covalent Bonds → High dissociation temperature

CHEMICAL NAMES: RULE 1

- **Simple compounds, composed of a metal and a non-metal, have the metal named first, followed by a slightly modified non-metal name.**
  - **The metal name is pronounced just as it would be for the pure metal.**
  - **The non-metal name has its ending changed to "ide".**

- **Examples:**

Formula	Chemical Name
MgO	Magnesium oxide
Al_2O_3	Aluminum* oxide
NaCl	Sodium chloride
$MgCl_2$	Magnesium chloride
ZnS	Zinc sulfide
Sb_2S_3	Antimony sulfide

* Note that the words Aluminum and Aluminium are both used throughout the world and by various organizations. In these notes, Aluminum is used.

CHEMICAL NAMES: RULE 2

- **When a metal atom is capable of combining in different proportions with the same non-metal atom, differentiation is accomplished using a Roman numeral to designate the "oxidation state" of the metal (discussed later).**
- **Examples:**

Formula	Chemical Name	Pre-IUPAC Name
CuCl	Copper(I) chloride	Cuprous chloride
$CuCl_2$	Copper(II) chloride	Cupric chloride
FeO	Iron(II) oxide	Ferrous oxide
Fe_2O_3	Iron(III) oxide	Ferric oxide
Fe_3O_4	Iron(II–III) oxide	Ferrosoferric oxide

- **IUPAC is the abbreviation for the International Union of Pure and Applied Chemistry. They have established a number of simplified naming conventions for chemicals.**

CHEMICAL NAMES: RULE 3

- **Some polyatomic ions (electrically charged groups of atoms called "Radicals") bond together well enough that the grouping often acts as if it were a single entity. Such a grouping is typically given its own special name.**
- **Examples:**

Radical	Formula	Chemical Name
CO_3^{2-}	$BaCO_3$	Barium "CARBONATE"
NO_3^-	KNO_3	Potassium "NITRATE"
ClO_3^-	$NaClO_3$	Sodium "CHLORATE"
NH_4^+	NH_4Cl	"AMMONIUM" chloride
SO_4^{2-}	$SrSO_4$	Strontium "SULFATE"
$C_2O_4^{2-}$	CaC_2O_4	Calcium "OXALATE"
HCO_3^-	$NaHCO_3$	Sodium "BICARBONATE"

- **More correctly HCO_3^- should be called hydrogen carbonate; thus $NaHCO_3$ should be called sodium hydrogen carbonate. However, its Pre-IUPAC name is still quite common.**

RADICALS COMMONLY FOUND IN PYROTECHNICS

Chemical Name	Formula
Ammonium	NH_4^+
Azide	N_3^-
Benzoate	$C_7H_5O_2^-$
Bicarbonate or Hydrogen carbonate	HCO_3^-
Carbonate	CO_3^{2-}
Chlorate	ClO_3^-
Dichromate	$Cr_2O_7^{2-}$
Fulminate	CNO^-
Nitrate	NO_3^-
Nitro	NO_2^0
Oxalate	$C_2O_4^{2-}$
Perchlorate	ClO_4^-
Peroxide	O_2^{2-}
Picrate	$C_6H_2N_3O_7^-$
Salicylate	$C_7H_5O_3^-$
Styphnate	$C_6HN_3O_8^{2-}$
Sulfate	SO_4^{2-}

CHEMICAL NAMES: RULE 4

- Natural organic substances and commercial products often use traditional and trade names, respectively. (One reason is that these substances often are not a single compound, rather they are mixtures of many different and complex compounds.)
- Examples:

Name	Natural Source	
Charcoal	The product of the destructive distillation of wood.	Natural
Dextrin	A modified (hydrolyzed) starch usually from corn or potatoes.	
Red gum	A resin obtained from Xanthorrhea bushes in Australia.	
Shellac	A resin collected from insects.	
Laminac™	Polyester and styrene monomer copolymer resins.	Commercial
Parlon™	Chlorinated rubber, available in various viscosities and grades.	
Viton™	Any of a series of fluoro-elastomer copolymers.	

CHEMICAL FORMULAS

- Chemical formulas are a shorthand notation:

Magnesium oxide	vs.	MgO
Potassium perchlorate	vs.	$KClO_4$

- They provide more information than a name:
  - Numbers of atoms (always shown).

    $NaCl$, H_2O, KNO_3

  - Groupings of atoms (sometimes shown).

    $Ba(NO_3)_2$, $Al_2(SO_4)_3$, $(NH_4)_2SO_4$

  - Charge of molecules or atoms (occasionally shown).

    Na^+, Cl^-, Fe^{2+}, NO_2^0

  - Physical state [solid (s), liquid (l) or gas (g)] (occasionally shown).

    $H_2O_{(s)}$, $Al_{(l)}$, $Mg_{(g)}$

CHEMICAL EQUATIONS

- Chemical equations are a shorthand notation:

  $$CuCl_2 \xrightarrow[H_2O]{} Cu^{2+} + 2\ Cl^-$$

  versus writing out:

  Copper(II) chloride dissolves in water to form a doubly-positive copper ion and two negatively charged chloride ions.

- They provide more information than the description of the chemical reaction:
  - Numbers of molecules or atoms (always shown).

    $$4\ Fe + 3\ O_2 \rightarrow 2\ Fe_2O_3$$

  - Special products or conditions (often shown).

    $$2\ Mg + O_2 \rightarrow 2\ MgO + \text{heat (15.0 kJ/g)}$$

    $$H_2O_{(s)} + \text{heat} \leftrightarrow H_2O_{(l)}$$

    $$BaCl^* \rightarrow BaCl + \text{photon (520 nm)}$$

    (* Indicates an excited electron state.)

RULES FOR CHEMICAL EQUATIONS

- Equations must be balanced with respect to:
  - Type and number of atoms.
  - Electric charge.
- Examples:
  - Number of oxygen atoms is not balanced:

    $KClO_3 + C \rightarrow KCl + CO_2$

    = Balanced:

    $2\ KClO_3 + 3\ C \rightarrow 2\ KCl + 3\ CO_2$
  - Charges are not balanced:

    $Na^0 + Cu^{2+} \rightarrow Na^+ + Cu^0$

    = Balanced:

    $2\ Na^0 + Cu^{2+} \rightarrow 2\ Na^+ + Cu^0$

STOICHIOMETRY

- In chemical equations, atoms and molecules are <u>COUNTED</u>. In chemical formulations, they are <u>WEIGHED</u>. “Stoichiometry” is the conversion between these two processes. Consider

  $Zn + S \rightarrow ZnS$

  - Does 1 atom of zinc react with 1 atom of sulfur?

    Yes
  - Should equal numbers of atoms be mixed to obtain a proper Zn/S formulation?

    Yes
  - Should equal <u>weights</u> of each be mixed?

    NO!
  - Why?

    Zinc atoms do not weigh the same as sulfur atoms.

ATOMIC WEIGHTS

- To find the relative weights of atoms, consult a table of "atomic weights". This gives the parts by weight that contain equal numbers of atoms.

Zn atomic weight is 65.4

S atomic weight is 32.1

- If these weights are expressed in grams, the number of atoms in each case is called a "mole".

$$Zn + S \rightarrow ZnS + \text{heat}$$

	Zn	S	ZnS
Atoms or molecules	1	1	1
Number of moles	1	1	1
Weight (*g*)*	65.4	32.1	
Total Weight	65.4 + 32.1 = 97.5		

(* Also parts by weight in kg, oz, lb, etc.)

Percent Zinc required: $\frac{65.4}{97.5} \times 100\% = 67.1\%$

Percent Sulfur required $\frac{32.1}{97.5} \times 100\% = 32.9\%$

SOME CHEMICAL ELEMENTS COMMONLY FOUND IN PYROTECHNICS

Name	Atomic Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	27.0
Antimony	Sb	51	121.8
Barium	Ba	56	137.3
Boron	B	5	10.8
Calcium	Ca	20	40.0
Carbon	C	6	12.0
Chlorine	Cl	17	35.5
Copper	Cu	29	63.5
Hydrogen	H	1	1.0
Iron	Fe	26	55.8
Lead	Pb	82	207.2
Magnesium	Mg	12	24.3
Nitrogen	N	7	14.0
Oxygen	O	8	16.0
Phosphorus	P	15	31.0
Potassium	K	19	39.1
Silicon	Si	14	28.1
Sodium	Na	11	23.0
Strontium	Sr	38	87.6
Sulfur	S	16	32.1
Titanium	Ti	22	47.9
Zinc	Zn	30	65.4
Zirconium	Zr	40	91.2

FORMULA WEIGHTS

- The "formula weight" (or molecular weight) of a substance is the sum of the atomic weights of each atom in the substance.
- Examples:
  - Formula weight of KNO_3

    = 1 (atomic weight of K) + 1 (atomic weight of N) + 3 (atomic weights of O)

    = 1 (39.1) + 1 (14.0) + 3 (16.0)

    = 101.1 is the formula weight.
  - Formula weight of $Ba(ClO_3)_2$

    = 1 (137.3) + 2 [1 (35.5) + 3 (16.0)]

    = 304.3 is the formula weight.

BLACK POWDER EXAMPLE

- One guess at the chemical equation for the burning of Black Powder is:

$$2\,KNO_3 + 3\,C + S \rightarrow K_2S + 3\,CO_2 + N_2$$

	KNO_3	C	S
Atoms or molecules	2	3	1
Number of moles	2	3	1
Weight (*g*)*	2 (101.1)	3 (12.0)	1 (32.1)
	= 202.2	= 36.0	= 32.1
Total weight	202.0 + 36.0 + 32.1 = 270.3		

(* Also parts by weight in kg, oz, lb, etc.)

Percent potassium nitrate: $\frac{202.2}{270.3} \times 100\% = 74.8\%$

Percent carbon: $\frac{36.0}{270.3} \times 100\% = 13.3\%$

Percent sulfur: $\frac{32.1}{270.3} \times 100\% = 11.9\%$

DIFFICULTIES WITH STOICHIOMETRIC APPROACH

- When the chemical equation is unknown, or cannot be guessed, stoichiometry is of little value.
- Reactions are often more complex than given by a single simple equation. Consider the products of burning Black Powder according to Davis.

(%)	Gases	(%)	Solids
26.3	Carbon dioxide (CO_2)	34.1	Potassium carbonate (K_2CO_3)
11.2	Nitrogen (N_2)	8.4	Potassium sulfate (K_2SO_4)
4.2	Carbon monoxide (CO)	8.1	Potassium sulfide (K_2S)
1.1	Water vapor (H_2O)	4.9	Sulfur (S)
1.1	Hydrogen sulfide (H_2S)	0.2	Potassium nitrate (KNO_3)
0.1	Methane (CH_4)	0.1	Potassium thiocyanate (KSCN)
0.1	Hydrogen (H_2)	0.1	Ammonium carbonate ($(NH_4)_2CO_3$)
		0.1	Carbon (C)
44.1	Gases	56.0	Solids

- Compare the chemical products from Davis with the previous Black Powder example.
  - $2\ KNO_3 + 3\ C + S \rightarrow K_2S + 3\ CO_2 + N_2$
  - Quite different!

SOME COMMON OXIDIZERS

Name	Formula	Notes
Ammonium perchlorate	NH_4ClO_4	Composite rockets, strobes
Barium chlorate	$Ba(ClO_3)_2$	Green color agent
Barium chromate	$BaCrO_4$	Delay columns / fuses
Barium nitrate	$Ba(NO_3)_2$	Green color agent
Barium peroxide	BaO_2	Tracers
Copper(II) oxide	CuO	Goldschmidt reactions
Guanidine nitrate	$(CH_6N_3)NO_3$	Gas production
Hexachloroethane	C_2Cl_6	HC smokes
Iron(II–III) oxide (black)	Fe_3O_4	Thermite
Iron(III) oxide (red)	Fe_2O_3	Thermite
Lead oxide (red)	Pb_3O_4	Prime, crackling microstars
Potassium chlorate	$KClO_3$	More common in past
Potassium dichromate	$K_2Cr_2O_7$	Burn catalyst, Mg coating
Potassium nitrate	KNO_3	Very commonly used
Potassium perchlorate	$KClO_4$	Very commonly used
Sodium chlorate	$NaClO_3$	Oxygen generator
Sodium nitrate	$NaNO_3$	Yellow color agent
Strontium nitrate	$Sr(NO_3)_2$	Red color agent
Strontium peroxide	SrO_2	Tracers
Sulfur	S	Hobby rocket propellant
Teflon™	$(C_2F_4)_n$	Infra red (IR) decoy flares

SOME COMMON COLOR AGENTS

SOME COMMON FUELS

Name	Formula	Notes
Aluminum	Al	Flash powder, white sparks
Antimony sulfide	Sb_2S_3	Flash powder, glitter
Boron	B	Delays
Charcoal	"C"	≈85% carbon
Ferroaluminum	Fe/Al	Sparks, typical alloy 35:65
Ferrotitanium	Fe/Ti	Sparks, typical alloy 30:70
Hexamine	$C_6H_{12}N_4$	Hexamethylenetetraamine
Iron	Fe	Branching sparks
Lactose	$C_{12}H_{24}O_{12}$	Low energy fuel
Lampblack	C	Gold sparks
Magnalium	Mg/Al	Many uses, typical alloy 50:50
Magnesium	Mg	Flame brightening
Potassium benzoate	$KC_7H_5O_2$	Whistles, whitish flame
Red gum	Complex	Acaroid resin
Silicon	Si	Makes SiO_2 in primes
Sodium benzoate	$NaC_7H_5O_2$	Whistles, yellow flame
Sodium salicylate	$NaC_7H_5O_3$	Whistles, yellow flame
Stearic acid	$C_{18}H_{36}O_2$	Low energy fuel
Sulfur	S	Black Powder
Titanium	Ti	White sparks
Wood meal	Complex	Mostly cellulose, lances
Zinc	Zn	Hobby rocket fuel
Zirconium	Zr	Primes, delays

SOME COMMON COLOR AGENTS

Name	Formula	Notes
Barium carbonate	$BaCO_3$	Green, neutralizer
Barium chlorate	$Ba(ClO_3)_2$	Green, oxidizer
Barium nitrate	$Ba(NO_3)_2$	Green, oxidizer
Barium sulfate	$BaSO_4$	Green
Calcium carbonate	$CaCO_3$	Reddish orange
Calcium sulfate	$CaSO_4$	Reddish orange
Copper(I) chloride	CuCl	Blue
Copper(II) carbonate	$CuCO_3$	Blue
Copper(II) oxide	CuO	Blue
Copper(II) oxychloride	$CuCl_2 \cdot 3Cu(OH)_2$	Blue
Cryolite	Na_3AlF_6	Yellow
Sodium nitrate	$NaNO_3$	Yellow, oxidizer
Sodium oxalate	$Na_2C_2O_4$	Yellow
Sodium sulfate	Na_2SO_4	Yellow
Strontium carbonate	$SrCO_3$	Red
Strontium nitrate	$Sr(NO_3)_2$	Red, oxidizer
Strontium oxalate	SrC_2O_4	Red
Strontium sulfate	$SrSO_4$	Red

- Sulfates and oxides often act as high temperature oxidizers in the presence of reactive metal fuels.

SOME COMMON BINDERS AND CHLORINE DONORS

BINDERS		
Name	Formula	Notes
CMC	$NaC_8H_{12}O_5$	Sodium carboxy-methyl cellulose
Dextrin	$(C_6H_{10}O_5)_n$	Approximate formula
Gum Arabic	Complex	Natural mixture
Laminac™	Variable	Polyester and styrene copolymers
Nitrocellulose	$(C_6H_7N_3O_{11})_n$	Also called cellulose nitrate
Red gum	Complex	Natural mixture / Acaroid resin
Rice starch	$(C_6H_{10}O_5)_n$	Approximate formula
Shellac	Complex	Natural mixture
Viton™	Variable	Fluoroelastomer copolymer

CHLORINE DONORS		
Name	Formula	Notes
Calomel	Hg_2Cl_2	15% chlorine
Chlorowax™	Variable	70% chlorine
Dechlorane™	$C_{10}Cl_{12}$	78% chlorine
Hexachlorobenzene	C_6Cl_6	75% chlorine
Parlon™	$(C_5H_6Cl_4)_n$	68% chlorine
Polyvinyl chloride	$(C_2H_3Cl)_n$	57% chlorine
Saran™ resin	$(C_2H_2Cl_2)_n$	73% chlorine

SOME OTHER CHEMICALS COMMONLY USED IN PYROTECHNICS

Name	Formula	Notes
Acetone	C_3H_6O	Nitrocellulose solvent
Boric acid	H_3BO_3	Neutralizer / buffer
Cab-O-Sil™	SiO_2	Flow agent
Diatomaceous earth	Mostly SiO_2	Inert filler
Dioctyl adipate	$C_{22}H_{42}O_4$	Plasticizer
Isopropanol	C_3H_8O	Solvent
Magnesium carbonate	$MgCO_3$	Glitter delay agent
Manganese dioxide	MnO_2	Burn catalyst / oxidizer
Methanol	CH_4O	Natural resin solvent
Methylene chloride	CH_2Cl_2	Polystyrene solvent
Methyl ethyl ketone (MEK)	C_4H_8O	Solvent
Oils	Various	Lubricant for pressing
Sodium bicarbonate	$NaHCO_3$	Neutralizer / glitter delay
Sodium silicate	$Na_2Si_4O_9$	Adhesive ingredient
Tetrahydrofuran (THF)	C_4H_8O	PVC solvent
Zinc oxide	ZnO	Adhesive ingredient

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SECTION 2

PYROTECHNIC CHEMISTRY, IGNITION AND PROPAGATION

- Oxidation States and Oxidation Numbers
- Oxidation–Reduction Reactions
- Pyrotechnic Compositions
- Pyrotechnic Reaction Energy Considerations
- Pyrotechnic Ignition
- Pyrotechnic Propagation

OXIDATION STATES / OXIDATION NUMBERS

- Oxidation state is a concept used to help understand pyrotechnic chemical reactions. It is an indication of the effective charge on an atom, or a way of assigning ownership to bonding electrons.

- Rules for oxidation states:

  - Uncombined atoms and atoms in molecules consisting of only one type of atom, have an oxidation state of zero, for example:

Na	Oxidation number (0)
Al	Oxidation number (0)
O_2	Oxidation number (0)
H_2	Oxidation number (0)

  - Atomic ions have an oxidation state equal to their charge, for example:

Na^+	Oxidation number (+1)
Al^{3+}	Oxidation number (+3)
O^{2-}	Oxidation number (–2)
Cl^-	Oxidation number (–1)

OXIDATION STATES / OXIDATION NUMBERS
(Continued)

- Rules for oxidation states (Continued):
  - In compounds or radicals, oxygen is always assigned the oxidation number of –2, and hydrogen is assigned a +1. All other atoms are assigned the values necessary to balance the charge of the compound, for example:

Water	H_2O
Oxygen	Oxidation number (–2)
Hydrogen (each)	Oxidation number (+1)
Methane	CH_4
Hydrogen (each)	Oxidation number (+1)
Carbon	Oxidation number (–4)
Chlorate ion	ClO_3^-
Oxygen (each)	Oxidation number (–2)
Chlorine	Oxidation number (+5)
Perchlorate ion	ClO_4^-
Oxygen (each)	Oxidation number (–2)
Chlorine	Oxidation number (+7)

OXIDATION–REDUCTION REACTIONS

- Pyrotechnic reactions are one type of oxidation-reduction reactions.

- Oxidation–Reduction Reactions — Chemical reactions in which reactants undergo PAIRED CHANGES in their oxidation states. (They may be called Redox and Electron Transfer Reactions.)

- Oxidation occurs when there is a loss of electrons (LEO) by an atom. This produces an algebraic increase in its oxidation state. For example:

$$Zn^0 \rightarrow Zn^{2+} + 2\ e^-$$

- Reduction occurs when there is a gain of electrons (GER) by an atom. This produces an algebraic decrease in its oxidation state. For example:

$$S^0 + 2\ e^- \rightarrow S^{2-}$$

- It is a paired change because something cannot be oxidized unless something else is reduced at the same time. That is to say, both of the above reactions must take place at the same time and place.

$$\underset{(0)}{Zn} + \underset{(0)}{S} \rightarrow \underset{(+2)(-2)}{ZnS}$$

EXAMPLES OF REDOX REACTIONS

- **Battery:**

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} + \text{Electricity}$$

(0) (+2) (+2) (0)

Zinc is oxidized – loses 2 electrons.
Copper is reduced – gains 2 electrons.

- **Electrolysis:**

$$2\ NaCl_{(l)} + \text{Electricity} \rightarrow 2\ Na_{(l)} + Cl_{2(g)}$$

(+1)(–1) (0) (0)

Sodium is reduced – gains 1 electron.
Chlorine is oxidized – loses 1 electron.

- **Combustion:**

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O + \text{heat}$$

(–4)(+1) (0) (+4)(–2) (+1)(–2)

Carbon is oxidized – loses 8 electrons.
Oxygen is reduced – gains 2 electrons.
Hydrogen is unchanged.

PYROTECHNIC COMBUSTION REACTIONS

- Pyrotechnic combustion differs from normal combustion in that the source of oxygen is not from the air, but rather it is from oxygen rich inorganic salts.

- General chemical equation (exothermic):

$$\text{Oxidizer} + \text{fuel} \rightarrow \text{products} + \text{heat}$$

  - The oxidizer and fuel combination is sometimes referred to as a "pyrogen".

  - Flash powder:

$$3\ KClO_4 + 8\ Al \rightarrow 3\ KCl + 4\ Al_2O_3 + \text{heat}$$

(+7) (0) (-1) (+3)

Chlorine is reduced – gains 8 electrons.
Aluminum is oxidized – loses 3 electrons.
Oxygen and potassium are unchanged.

  - Thermite:

$$Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe + \text{heat}$$

(+3) (0) (+3) (0)

Iron is reduced – gains 3 electrons.
Aluminum is oxidized – loses 3 electrons.
Oxygen is unchanged.

OXIDIZER DECOMPOSITION
[SHIDLOVSKIY & SHIMIZU]

- **Potassium Nitrate:**

  $2\ KNO_3 \rightarrow 2\ KNO_2 + O_2 \rightarrow K_2O + N_2 + 5/2\ O_2$

  (This 2 step process is similar for other metal nitrates.)

- **Potassium Perchlorate:**

  $KClO_4 \rightarrow KCl + 2\ O_2$

  (Similar for $KClO_3$.)

- **Ammonium Perchlorate:**

  $2\ NH_4ClO_4 \rightarrow 3\ H_2O + N_2 + + 2\ HCl + 5/2\ O_2$

- **Iron Oxide (Red):**

  $Fe_3O_4 \rightarrow 3\ Fe + 2\ O_2$

  (Similar for other metal oxides.)

TYPICAL FUEL OXIDATION

- **Aluminum and Magnesium:**

  $4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$

  $2\ Mg + O_2 \rightarrow 2\ MgO$

  (Similar for other metals – considering ionic charges.)

- **Carbon and Sulfur:**

  $C + O_2 \rightarrow CO_2$

  (forms CO if insufficient O_2.)

  $S + O_2 \rightarrow SO_2$

- ***Stearic Acid:***

  $C_{18}H_{36}O_2 + 26\ O_2 \rightarrow 18\ H_2O + 18\ CO_2$

  - **Oxygen first reacts with hydrogen to form water.**
  - **Oxygen next reacts with carbon to form CO.**
  - **If sufficient oxygen, it then reacts to form CO_2.**

  (Similar for other organic compounds.)

ESTIMATING REACTION PRODUCTS

- Although neither completely accurate nor reliable, the information about oxidizer decomposition and fuel oxidation can be used to estimate reaction products.
- For example, consider the case of magnesium photo flash powder
  - Combine (add together) the reactions given previously, in the ratio that causes the number of oxygen atoms to be the same for both reactions

$$\begin{array}{l} KClO_4 \rightarrow KCl + 2\,O_2 \\ 4\,Mg + 2\,O_2 \rightarrow 4\,MgO \\ \hline KClO_4 + 4\,Mg + 2\,O_2 \rightarrow KCl + 2\,O_2 + 4\,MgO \end{array}$$

  - Cancel the free oxygen on both sides of the equation for the likely reaction.

$$KClO_4 + 4\,Mg \rightarrow KCl + 4\,MgO$$

NON-OXYGEN PYROTECHNIC OXIDIZERS

- Other highly electronegative elements can take the place of oxygen and function as an oxidizer (electron acceptor) in pyrotechnic reactions.
- Examples:
  - Rocket fuel, using sulfur as oxidizer:

$$\underset{(0)}{S} + \underset{(0)}{Zn} \rightarrow \underset{(+2)(-2)}{ZnS} + \text{heat}$$

Sulfur is reduced – gains 2 electrons.
Zinc is oxidized – loses 2 electrons.

  - Decoy flare, using fluorine compounds (PTFE):

$$(C_2F_4)_n + 2n\,Mg \rightarrow 2n\,C + 2n\,MgF_2 + \text{heat}$$

(PTFE is polytetrafluoroethylene and called Teflon™)

  - Screening smoke, using chlorine compounds:

$$C_2Cl_6 + 3\,Zn \rightarrow 3\,ZnCl_2 + 2\,C + \text{heat}$$

HIGH EXPLOSIVES: REDOX DECOMPOSITION

- **High explosive reactions are also redox reactions. However, because the oxidizer and fuel are combined *within the same molecule, their reactions can also be* considered decomposition reactions.**

- **High explosives are classed according to their ease of initiation. The three classes, in decreasing order of sensitivity to detonation, are:**

  - **Primary explosive (e.g., lead azide):**

$$\underset{(+2)}{\mathrm{Pb}}(\underset{(-2/3)}{\mathrm{N}_3})_2 \rightarrow \underset{(0)}{\mathrm{Pb}} + 3\ \underset{(0)}{\mathrm{N}_2} + \text{heat}$$

  - **Secondary explosive (e.g., nitroglycerin):**

$$4\ C_3H_5N_3O_9 \rightarrow$$
$$12\ CO_2 + 10\ H_2O + 6\ N_2 + O_2 + \text{heat}$$

  - **Blasting agent (a tertiary explosive) (e.g., "ANFO", ammonium nitrate fuel oil):**

    - **Ammonium nitrate can explosively decompose.**

$$2\ NH_4NO_3 \rightarrow 2\ N_2 + 4\ H_2O + O_2 + \text{heat}$$

    - **The additional fuel oil reacts with the excess oxygen.**

TYPICAL PYROTECHNIC COMPOSITIONS

- **They have reactions that are self-contained (do not rely upon atmospheric oxygen), are self-sustained (propagate throughout), and are exothermic (produce heat energy).**

- **They are physical mixtures of fuel(s) and oxidizer(s). (They are generally not chemical compounds as are high explosives.)**

- **They generally contain additives, such as binders, color agents, neutralizers, etc.**

- **They generally are composed of relatively small particles, 0.01 – 0.001 inch (0.25 – 0.025 mm) in diameter.**

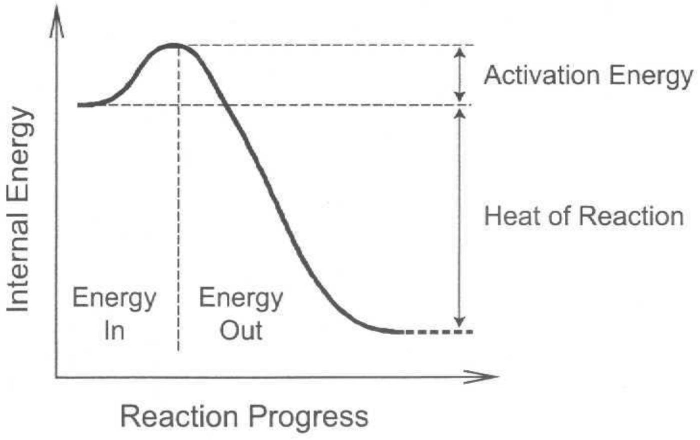
- **In most instances, they are low explosives, which can only burn or deflagrate upon ignition.**

RAMIFICATIONS OF PYROTECHNIC COMPOSITIONS BEING PHYSICAL MIXTURES OF SMALL PARTICLES

- For a pyrotechnic chemical reaction to occur, atoms must be in physical contact.
- Thus, at most, only atoms on the surface of particles are available to participate in reactions.
- Consider a 0.001 inch (0.025 mm) diameter particle:
  - It consists of about 10^{15} atoms (million billion).
  - Only about 1 atom in 30,000 is on the surface.
- Accordingly, under normal conditions, almost none of the fuel or oxidizer present is capable of participating in a pyrotechnic reaction.
  - This is the reason why pyrotechnic materials generally react very much slower than high explosives.

PYROTECHNIC REACTION ENERGY CONSIDERATIONS

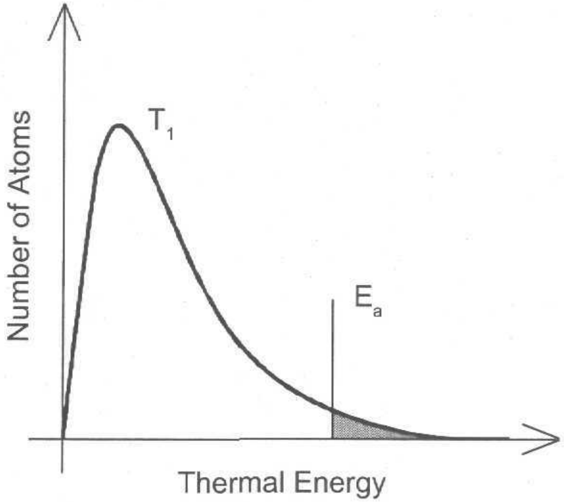
- In addition to the requirement that atoms must be in physical contact before they can react, they must possess sufficient energy to initiate the reaction.
- A pyrotechnic reaction can be considered as taking place in two steps. First, energy must be input to the system (“Activation Energy”). Second, energy is produced by the reaction (“Heat of Reaction” also more correctly called “Enthalpy of Reaction”).



- The first step can be thought of as the breaking of the original chemical bonds, and the second step, as forming of new and stronger chemical bonds.

THERMAL ENERGY DISTRIBUTION

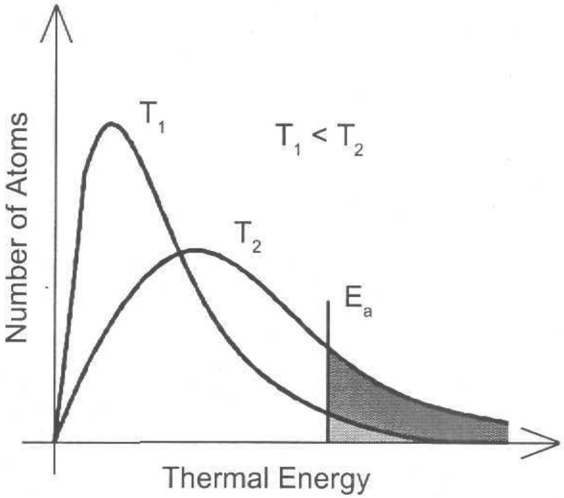
- At any given temperature, atoms have a distribution of thermal energies ranging from zero to very high energies. Thus a few of the atoms in a pyrotechnic composition have energies exceeding E_a, the activation energy necessary to react.



- Then why are not all pyrotechnic mixtures reacting continuously? They are, but only very, very slowly. The fraction of atoms exceeding E_a at room temperature is about 1 in 1,000,000,000,000. Only about 1 in 30,000 of these atoms are on the particle's surface, and the fraction of fuel and oxidizer surfaces in contact is about 1 in 20. As a result, only about 1 in 600,000,000,000,000,000 is capable of reacting.

EFFECT OF INCREASED TEMPERATURE ON THERMAL ENERGY DISTRIBUTION

- As temperature rises, the fraction of atoms with thermal energies exceeding the activation energy increases greatly.

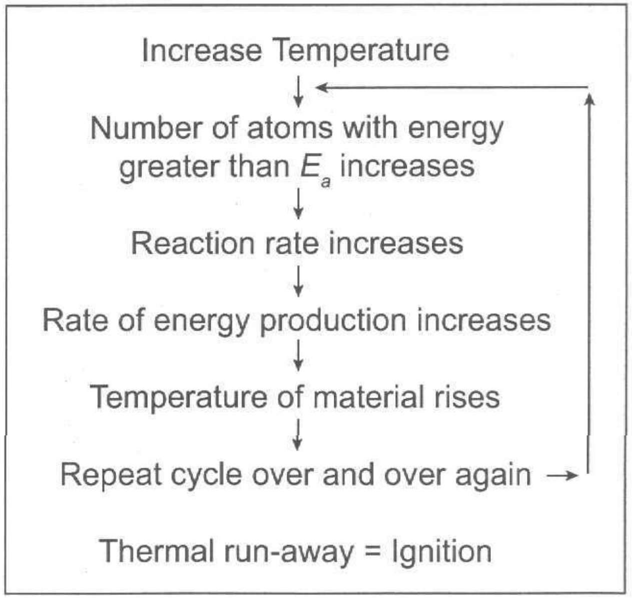


- The effect of raising the temperature is that the rate of reactions occurring at T_2 is much greater than at T_1, although it may still be very low.

- For Black Powder at 350 °C there are approximately 100,000,000 times as many molecules exceeding E_a as there are at room temperature. However, this is still only about one molecule in 10,000,000. [Smith]

EFFECT OF RISING TEMPERATURE

- **Whenever the temperature of a pyrotechnic composition rises, a series of consequences would seem to follow naturally:**



Increase Temperature

↓

Number of atoms with energy greater than E_a increases

↓

Reaction rate increases

↓

Rate of energy production increases

↓

Temperature of material rises

↓

Repeat cycle over and over again →

Thermal run-away = Ignition

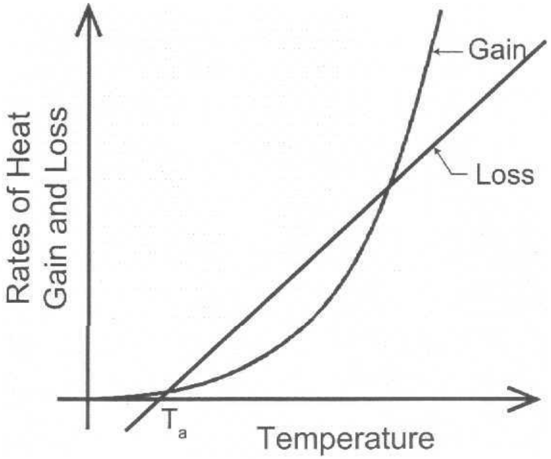
- **However, this is contrary to everyday observations; a slight rise in temperature generally does not eventually lead to pyrotechnic ignition.**

- **The reason is that only half of the picture, how heat is produced, has been considered. How heat is lost to the surroundings must also be addressed.**

MORE COMPLETE THERMAL PICTURE

- **As the temperature (T) of a pyrotechnic composition rises, the rate of heat production (R_{gain}) from thermal reactions increases exponentially, essentially following the Arrhenius equation, where A and B are constants and e = 2.718…:**

$$R_{gain} \approx Ae^{BT}$$

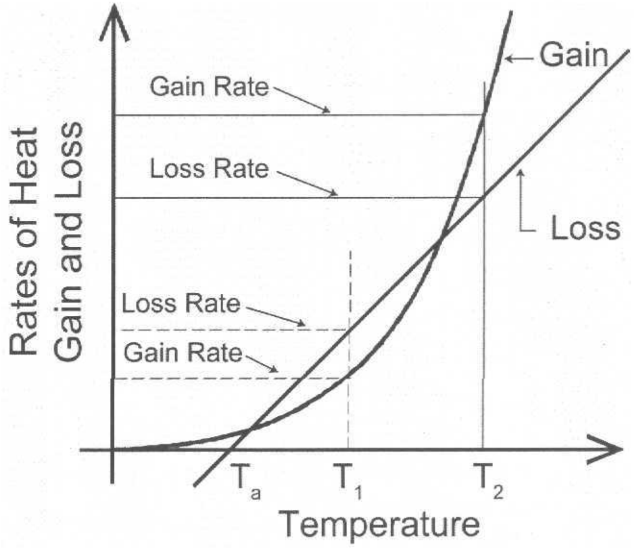


- **As temperature rises, in the range below several hundred degrees Celsius, the rate of heat loss (R_{loss}) to the surroundings, is roughly proportional to the temperature difference between the pyrotechnic composition (T) and the surroundings (T_a):**

$R_{loss} \approx k\,(T - T_a)$ **(where k is a constant).**

EFFECT OF RAISING TEMPERATURE (MORE COMPLETE VIEW)

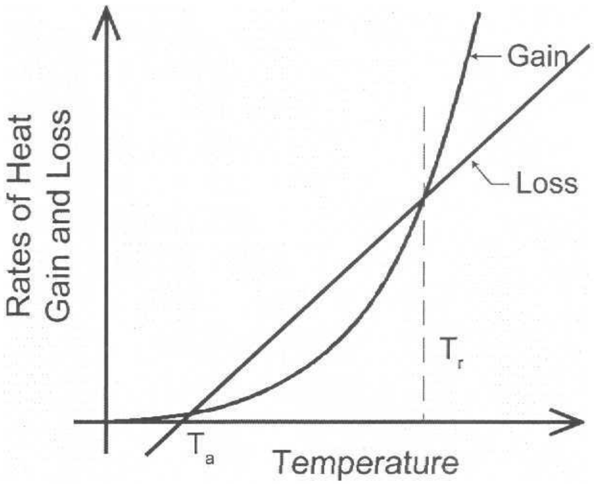
- If the temperature is raised to T_1, the rate of energy production and the rate of energy loss both increase. However, the rate of loss increases more than the rate of production. Thus the composition will cool back toward room temperature.



- If temperature is raised to T_2, above the crossing point of the curves, the temperature will continue to rise and at an accelerating rate. This is because the rate of production exceeds the rate of loss, and the difference between gain and loss increases rapidly as the temperature continues to rise.

THERMAL RUN-AWAY TEMPERATURE

- The temperature corresponding to the point where the 2 lines cross on the graph can be called the "Thermal Run-Away Temperature" (T_r).



- For a pyrotechnic composition, T_r depends on the E_a (Activation Energy), ΔH_r (Enthalpy of Reaction) and ease of heat loss.

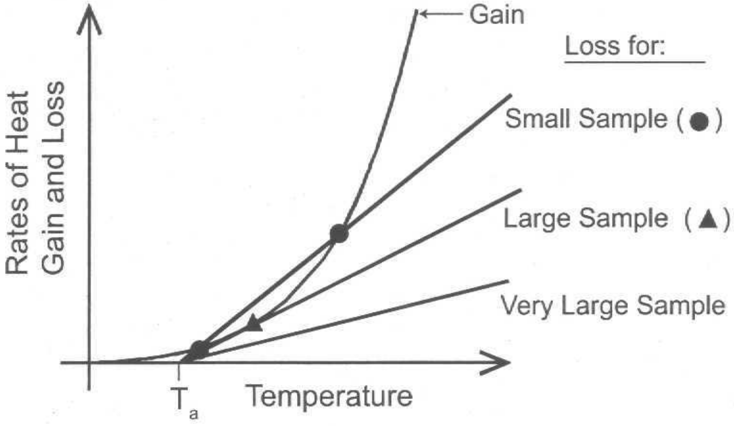
Low E_a → Low T_r

High ΔH_r → Low T_r

Much Composition → Low T_r

SAMPLE SIZE EFFECT

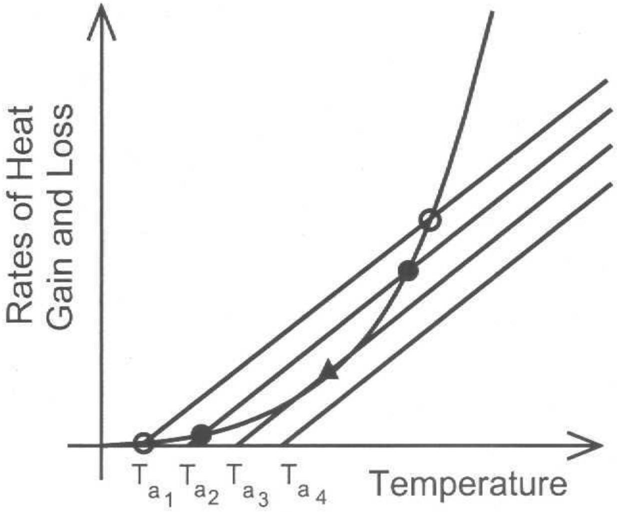
- **The rate of heat gain is not affected by sample size. However, the rate of heat loss is dependent on sample size because of a thermal insulating effect.**



- **If any pyrotechnic material is present in large enough quantity or is well enough insulated, the rate of heat gain will always be greater than the rate of heat loss. In that event, the sample will spontaneously ignite. (However, the time to ignition may be very, very long, and the quantity needed may be astronomically large.)**

AMBIENT TEMPERATURE EFFECT

- **The rate of heat gain is affected by sample temperature but not by ambient temperature. However, the rate of heat loss is affected by ambient temperature.**



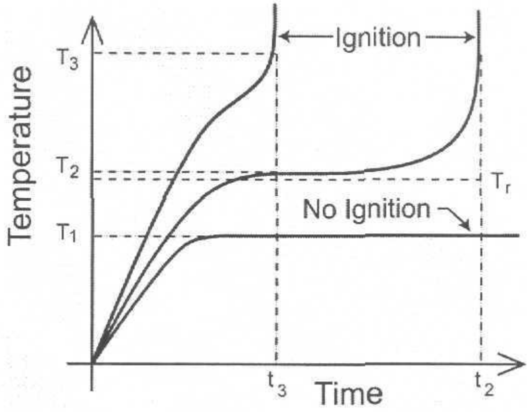
- **If any pyrotechnic material is placed in a sufficiently high temperature environment, thermal run-away will occur and an ignition will result.**

SPONTANEOUS IGNITION ACCIDENTS

- **Spontaneous ignition accident statistics from China reveal that** [Hao]**:**
  - **Most happen in geographic locations below 35° N Latitude.**
  - **Most happen during the months of July, August and September.**
  - **Most happen between 2 and 4 p.m. LDT.**
  - **Most happen on holidays or time off-duty.**
- **Thus, most spontaneous ignition accidents happen in hot and humid climates, during the hottest time of the year, at the hottest time of the day, and on days when areas are closed (minimum air exchange rate).**

TIME TO IGNITION

- **If a pyrotechnic composition is heated to any temperature (T_1) that is less than T_r, the time to ignition will be infinite (i.e., there will be no ignition).**



- **If a pyrotechnic composition is raised to a temperature (T_2), slightly above T_r, the time to ignition (t_2) may be long (hours or days), but ignition will occur.**
- **As a pyrotechnic composition is raised to temperatures more and more in excess of T_r (such as T_3), the time to ignition (t_3) becomes increasingly short, until it appears to be nearly instantaneous.**

IGNITION TEMPERATURES

IGNITION TEMPERATURE

- **Because thermal run-away temperature depends on ambient temperature and sample size, “Ignition Temperature” is used instead.**

- **Ignition temperature can be determined by several methods. Each produces slightly different values, but generally all are within a few degrees.**
  - **Hot Bath Method One: The lowest temperature of a bath of molten Wood’s metal that results in ignition within 5 minutes for a 0.1 g sample in a small glass test tube.**
  - **Hot Bath Method Two: Using a method similar to above, but with bath temperature increasing 5 °C per minute and using a ¼" thin-walled brass or aluminum tube. The temperature of the bath at the *time of ignition is reported as ignition temperature.***
  - **Hot Bath Method Three: With a series of bath temperatures near that required for ignition, measure the time taken for ignition as a function of bath temperature. Plot the results and extrapolate to zero time.**
  - **Differential Thermal Analysis: Temperature at the onset of the ignition exotherm, when sample temperature is raised at a rate of 50 °C per minute.**

IGNITION TEMPERATURES

- **Ignition temperature (T_i) of common pyrotechnic mixtures** [McIntyre, Conkling]:

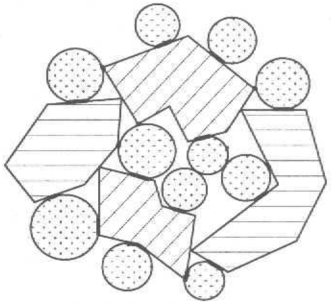
	T_i (°C)
– **Photo flash powder** **[$KClO_4$ + Al]**	**≈750**
– **Red star** **[Mg + $Sr(NO_3)_2$ + $KClO_4$ + + HCB + asphaltum]**	**≈500**
– **Green star** **[Mg + HCB + $Ba(NO_3)_2$]**	**≈450**
– **Black Powder** **[KNO_3 + charcoal + S]**	**≈350**
– **H3 (Break powder)** **[$KClO_3$ + charcoal]**	**≈350**
– **Smoke pyrogen** **[$KClO_3$ + lactose]**	**≈200**
– **$KClO_3$ + sulfur**	**≈150**

(Note T_i ≈ 120 °C for larger sample that was heated slowly). [Champan]

THE EFFECT OF MELTING ONE COMPONENT IN A PYROTECHNIC COMPOSITION

- When both fuel and oxidizer are solid particles, relatively little of their surfaces (i.e., fuel and oxidizer atoms) are actually in physical contact.

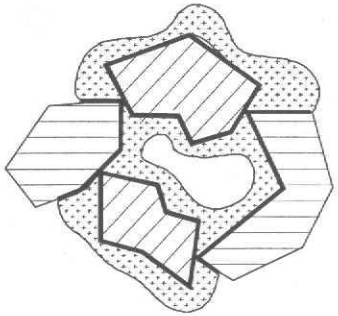
Before:



Very little surface in contact

- After one component melts, it is free to flow over the surface of the other components. Thus, the number of fuel and oxidizer atoms in physical contact is very much greater.

After:



Very much more surface in contact

EFFECT OF MELTING ON IGNITION

- When melting occurs:

The percentage of atoms in physical contact increases.

↓

More atoms with energies exceeding E_a will be in contact and will react.

↓

Rate of reaction increases.

↓

Rate of energy production increases.

↓

Thermal run-away (ignition) occurs at a slightly lower temperature.

- As a pyrotechnic composition is heated and is near its ignition temperature, if one of its components reaches its melting point, ignition will generally occur at that temperature.

For example, KNO_3 (Pure), T_m = 334 °C

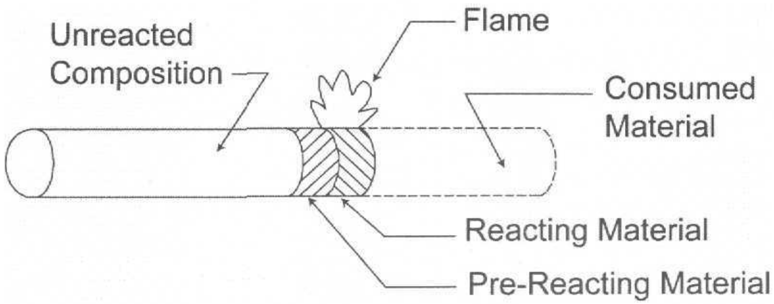
Black Powder (KNO_3 + Char. + S), $T_i \approx$ 330 °C (DTA)

PYROTECHNIC IGNITION IN SIMPLEST TERMS

- In the simplest of terms, ignition occurs when a pyrotechnic composition is raised to its ignition temperature.
- Why have we looked at ignition theory in such detail? Many pyrotechnic problems are really ignition problems, for example:
  - Accidental fires and explosions.
  - Premature functioning of devices.
  - Dud devices and components:
    - = Aerial fireworks shell.
    - = Signal flares and smokes.
- By better understanding details of the mechanism of ignition, it is more likely that one will be successful in managing (avoiding) such ignition problems.

SIMPLE MODEL OF PROPAGATION

- Once a portion of a pyrotechnic composition has been ignited, propagation (burning throughout) is not guaranteed.
- Heat is produced by the burning composition (reacting material). That heat is transferred to the surroundings (e.g., air, unburned composition, etc.). If enough heat is transferred to the next layer of unreacted composition (pre-reacting material) to raise that to the ignition temperature, burning will continue (propagate).



- Propagation can be thought of as “continuing self-ignition”.

THE LIKELIHOOD OF PROPAGATION

- Propagation Inequality (required for propagation):

Energy Fed Back > E_a

where E_a = Activation energy.

Energy Fed Back = $\Delta H_r \cdot F_{fb}$

where ΔH_r = Heat (Enthalpy) of reaction and
F_{fb} = Fraction fed back.

- Thus propagation inequality is:

$$\Delta H_r \cdot F_{fb} > E_a$$

- Factors maximizing the likelihood of propagation:

1. Low ignition temperature (i.e., low activation energy, E_a).
2. Much heat produced (i.e., high heat of reaction, ΔH_r).
3. Efficient energy feedback from reacting to pre-reacting material (i.e., large fraction of energy is fed back, F_{fb}).

MECHANISMS OF ENERGY FEEDBACK

- Conduction:
  - Thermal energy (molecular vibration) is conducted along solids, from hotter to cooler. Factors maximizing conductive feedback:

    = Compacted composition.

    = Metal fuels.

    = Metal casing / core wire.

- Convection:
  - Hot gases penetrate the solid composition along spaces between grains (fire paths). Factors maximizing convective feedback:

    = Uncompacted composition.

    = Granulated composition.

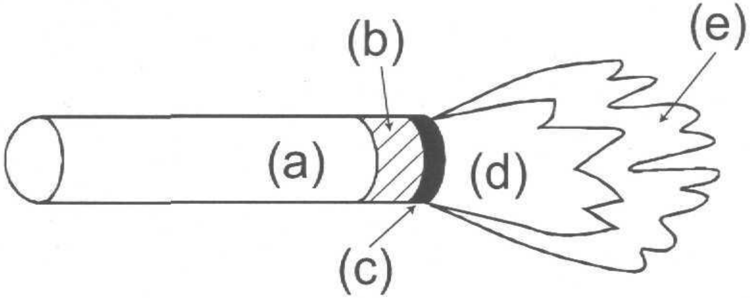
- Radiation:
  - Thermal (infrared) radiation, emitted from flame and glowing particles, is absorbed by incompletely reacted composition. Factors favoring radiative feedback:

    = Solid or liquid particles in the flame.

    = Dark or black composition.

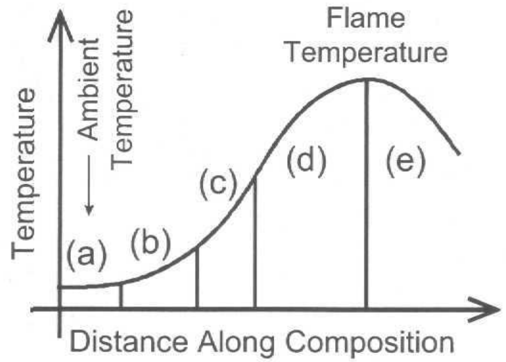
BURNING PYROTECHNIC COMPOSITION

- **More complete model of propagation:**



(a) Unreacted pyrotechnic composition,
(b) Warm-up zone (possible solid state reactions),
(c) Reaction in condensed phase (at least one liquid phase),
(d) Reaction in gaseous phase (liquid droplets possible), and
(e) Reaction complete, combustion products are cooling.

- **Temperature Profile:**



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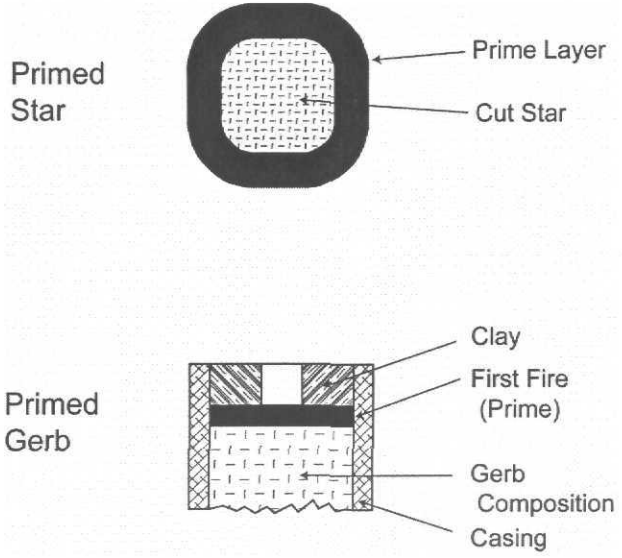
SECTION 3

PYROTECHNIC PRIMES AND PRIMING

- **Pyrotechnic Primes**
- **Shimizu Energy Diagrams**
- **Ignition and Propagation Problems**
- **Prime Formulations**
- **Priming Techniques**
- ***Alternatives to Priming***

PYROTECHNIC PRIME

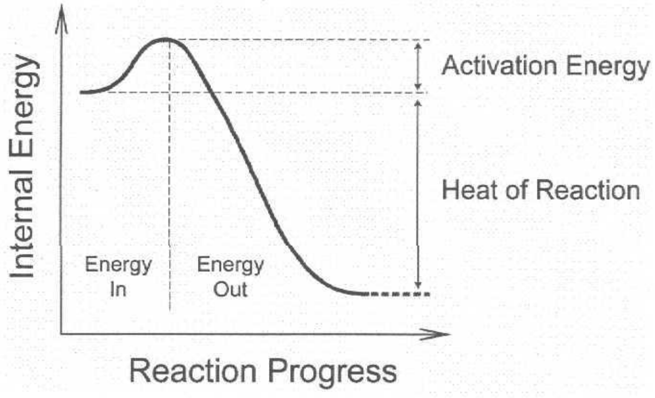
- **Pyrotechnic prime — A composition used to enhance the probability of successful ignition of another pyrotechnic material.**



- **A prime may be referred to by the descriptive term “first fire”.**

PYROTECHNIC PRIME

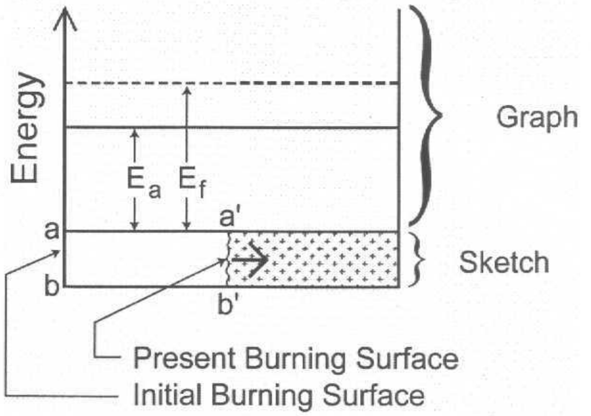
- Characteristics of a good prime:
  - Easily ignited (E_a is low).
  - Generates abundant thermal energy (ΔH_r is high).
  - Not overly sensitive to accidental ignition (E_a is not <u>too</u> low).



- Efficient energy feedback, for example:
  - = Thermally conductive,
  - = Dark colored (black), or
  - = Generates molten slag.

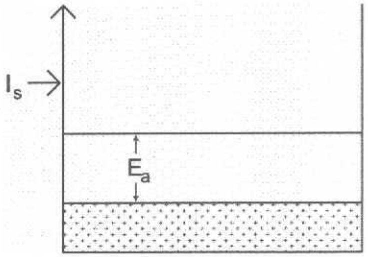
SHIMIZU ENERGY DIAGRAMS

- E_a = Activation energy, the amount of energy needed to ignite a tiny sample of pyrotechnic composition.
- ΔH_r = Heat of reaction, the amount of energy produced by a tiny sample of pyrotechnic composition.
- E_f = Energy feedback, the amount of energy produced by a pyrotechnic composition that is fed back to the unburned composition.
- Thus $E_f = \Delta H_r \cdot F_{fb}$, where F_{fb} is the fraction of energy fed back.



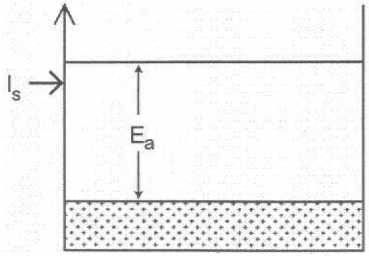
SHIMIZU ENERGY DIAGRAMS — IGNITION

- Activation energy is low and ignition stimulus (I_s) is substantially greater than E_a:



  - Composition will be easily ignited by stimulus I_s. (Accidental ignition is a possibility.)

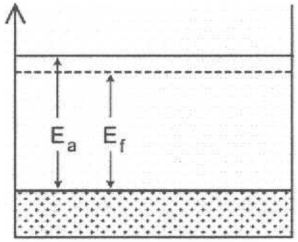
- Activation energy is high and ignition stimulus is less than E_a:



  - Composition will not be ignited by I_s.

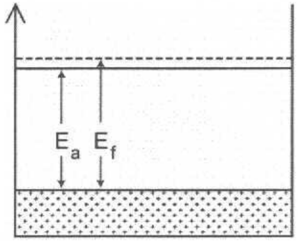
SHIMIZU DIAGRAMS — PROPAGATION

- Energy fed back (E_f) is less than the activation energy (E_a).



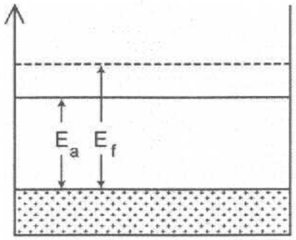
  - Composition will not propagate. It may react under heavy ignition stimulus, but will extinguish upon removal of the stimulus.

- Energy fed back is slightly greater than the activation energy.



  - Composition will propagate weakly but can be easily extinguished.

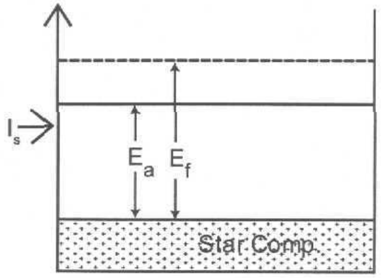
- Energy fed back is significantly greater than the activation energy.



  - Composition will propagate vigorously and will be difficult to extinguish.

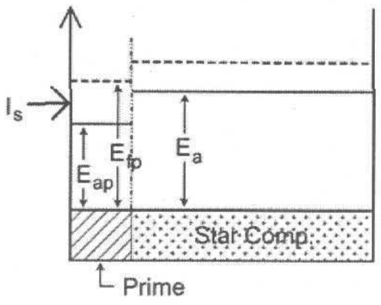
SHIMIZU DIAGRAM FOR STAR OR FLARE COMPOSITION

- **Unprimed star (or flare):**



- Star composition would propagate (burn) if ignited, but stimulus is not sufficient for ignition ($I_s < E_a$).

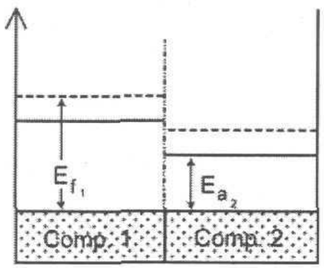
- **Primed star (or flare):**



- Prime is ignited by stimulus ($I_s > E_{ap}$) and the burning prime ignites the star composition ($E_{fp} > E_a$).

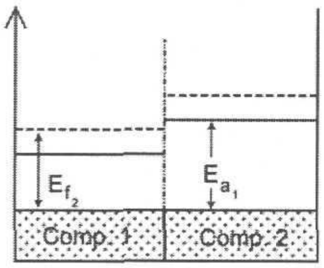
SHIMIZU DIAGRAMS — COLOR CHANGE STAR

- **Successful color change star:**



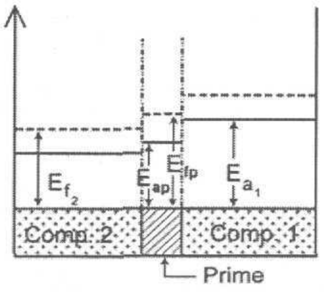
- Burning (from left to right) propagates through the contact between the two compositions, consuming both completely ($E_{f1} > E_{a2}$).

- **Unsuccessful color change star:**



- Burning fails to propagate past the contact between the two compositions, leaving composition 1 unburned ($E_{f2} < E_{a1}$).

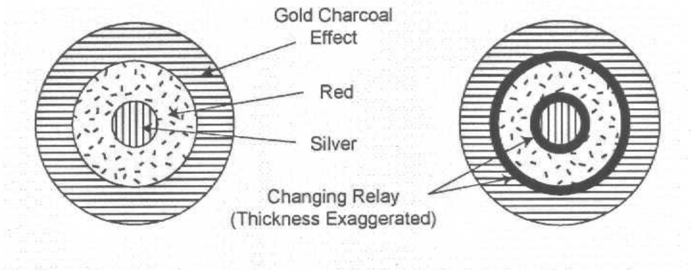
- **Prime used for successful color change:**



- Burning propagates through both contacts, consuming all compositions ($E_{f2} > E_{ap}$ and $E_{fp} > E_{a1}$). (Prime could be 50:50 mix of compositions 1 and 2.)

COLOR-CHANGE RELAY OR DARK PRIME

- **Color-change relay or dark prime (used in fireworks) has good ignition characteristics, plus it burns without producing much visible light.**



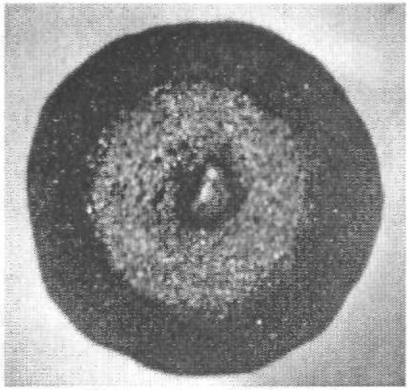
No Prime Between Layers

Dark Prime Between Layers

- **In addition to facilitating complete burning, there is an aesthetic advantage to using the color-change relay.**
  - **Because of slight differences in ignition, burn rate, and size of individual stars, all will not change color at precisely the same time.**
  - **At the boundary between two colors, colors produced will generally be less attractive than either star color.**
  - **The dark burning period causes a group of stars to appear more nearly to all change color simultaneously and cleanly.**

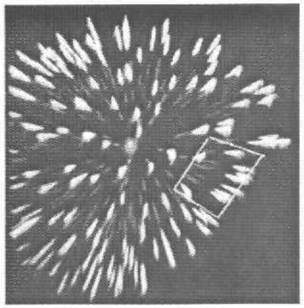
COLOR CHANGE RELAY – DARK PRIME (Continued)

- **Example of color change star with no apparent dark prime layers.**



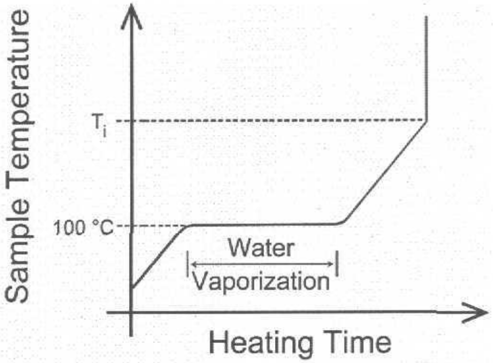
(Photo courtesy of R. Winokur)

- **Observe that little or no light is produced when the dark prime burns between the color changes for these stars.**

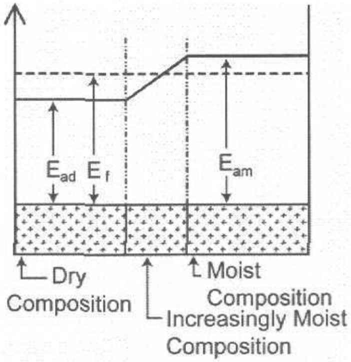


PROBLEM WITH MOIST COMPOSITIONS

- Energy is required to drive off moisture, which must occur before ignition temperature can be reached.



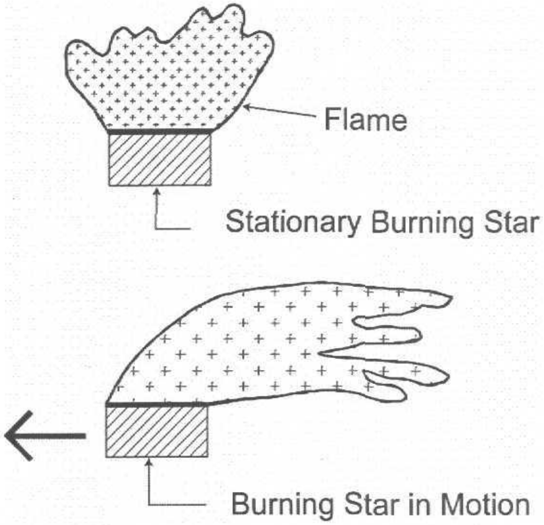
- Propagation failure for partially dry star:



- In effect, the presence of moisture increases E_a. When $E_a > E_f$, burning ceases.

EFFECT OF STAR MOTION THROUGH AIR

- Stationary and moving pellets of composition (fireworks stars, flares, tracers, etc.)



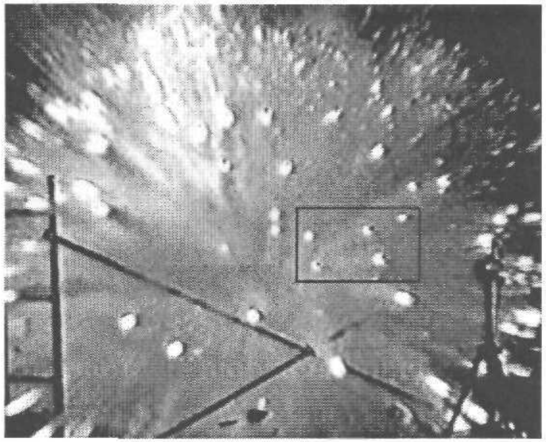
- The star moves away from the flame, which trails after it. The result is that the fraction of energy fed back (F_{fb}) is reduced.

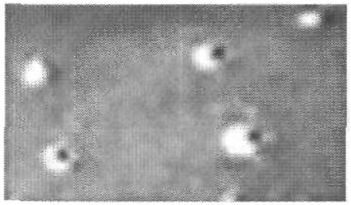
$$E_f = \Delta H_r \cdot F_{fb}$$

- Thus the amount of energy fed back (E_f) is lowered, and the amount of lowering is a function of the speed at which the star is traveling.

EXAMPLE OF STARS IN MOTION

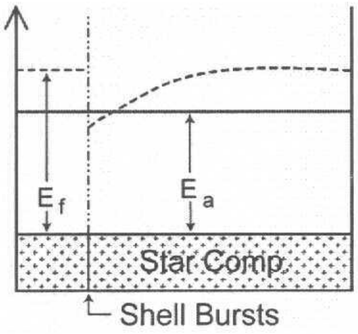
- ***View and close-up view of a fireworks shell burst.*** **Notice how the flame is following behind the stars.**





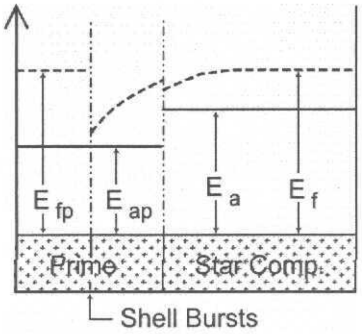
EFFECT OF MOTION ON COMPOSITION BURNING

- **Unprimed stars may be extinguished ("blown blind").**



- **Star is extinguished when shell bursts because the initial high velocity of the star causes E_f to momentarily fall below E_a.**

- **Primed stars — stay ignited.**

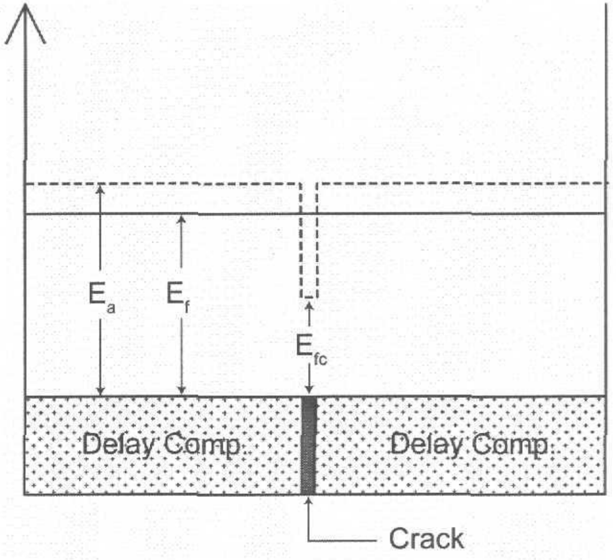


- **Star (prime) continues burning even as shell bursts because, while E_{fp} drops, it never falls below E_{ap}. By the time the prime burns out, the velocity of the star is low enough to stay lit ($E_{fp} > E_a$ and $E_f > E_a$).**

- **Analogous for flares and tracers, etc.**

CRACK IN GASLESS COMPOSITON

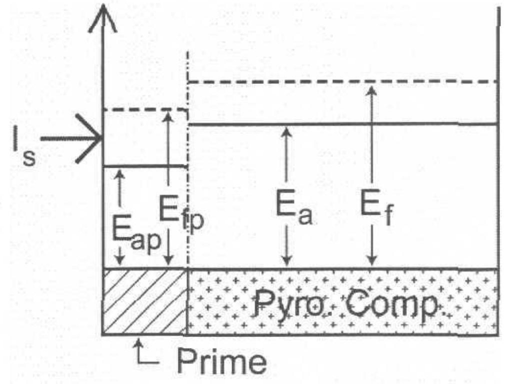
- Delay compositions often have gasless reactions, which rely heavily on conductive energy feedback for propagation. A crack through the composition seriously reduces the amount of thermal energy fedback and can result in a failure to propagate.



- Cracks can result from temperature or humidity cycling. They can also occur when pressing into elastic containers, that contract when the pressure is released.

REVIEW: CHARACTERISTICS OF A GOOD PRIME

- A good prime:
  - Ignites easily (E_a is low).
  - Is not overly sensitive to accidental ignition (E_a is not <u>too</u> low).
  - Generates abundant thermal energy (ΔH_r is high).
  - Has efficient energy feedback mechanisms.
    - = Is thermally conductive.
    - = Generates molten slag, not solids or gases.



BLACK POWDER AND ROUGH POWDER PRIME

- **Uses: General priming for flares, stars, gerbs and fuse.**
- **In military and some fireworks applications, commercial Black Powder is used.**
- **In most fireworks applications, handmade or rough Black Powder is used.**

Ingredient	Normal*	Enhanced**
Potassium nitrate	75	75
Charcoal (air float)	15	15
Sulfur	10	10
Silicon (–325 mesh)	—	+10

* Inexpensive, effective, handmade prime.

** Upon burning, this prime produces more thermal energy and molten particles of SiO_2 (glass).

POTASSIUM PERCHLORATE PRIME FORMULATIONS

- **Uses: Priming of ammonium perchlorate compositions (when potassium nitrate-based prime must not be used), or when sulfur may need to be avoided (possibly when chlorate oxidizers are used).**

Ingredient	Normal	Easy Ignition*
Potassium perchlorate	70	70
Accroides (red) gum	20	20
Charcoal (air float)	10	10
Potassium dichromate**	—	+5

* Has lower ignition temperature. Is more resistant to high wind velocity.

** Warning: Potassium dichromate has a Health Safety Rating of 4 (Extreme).

SPECIAL PRIMES

- Examples:

Ingredient	Dark Prime (a)	Starter Mixture (b)	Thermite Igniter (c)
Potassium nitrate	76	35	—
Potassium perchlorate	7	—	—
Barium peroxide	—	—	31
Iron oxide (black)	—	22	29
Antimony sulfide	3	—	—
Accroides (red) gum	2	—	—
Charcoal (air float)	8	4	—
Aluminum (fine)	—	13	40
Silicon	—	26	—
Reference	Shimizu	Ellern	Ellern

(a) Dark prime is used as a color-change relay in fireworks. It emits little or no visible light.

(b) Starter mixture was used to produce the high temperatures needed to ignite HC smokes.

(c) Thermite igniter is a modified thermite itself, with easier ignition characteristics.

PRIME BINDING METHODS

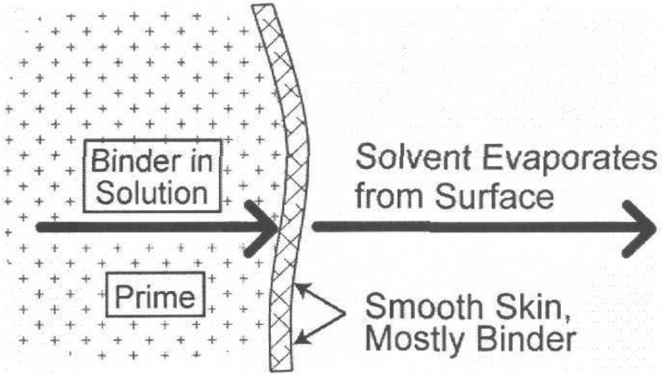
- Method I. Use +5% dextrin and add water to achieve desired consistency (becomes faster drying if used with 50:50 water:alcohol mixture). Water migration into fuse can be a problem.
- Method II. Add 10% solution of nitrocellulose lacquer to achieve desired consistency (can be thinned using acetone) (very fast drying).
- Method III. Use alcohol to activate red gum or other alcohol soluble component as the binder (only if the prime contains sufficient red gum or other alcohol soluble component).
- Method IV. Use pressure to cause plastic flow binding. Components such as sulfur, red gum or asphaltum will act as binder under pressure (only useful for pressed items).

PRIME APPLICATION TECHNIQUES

- **Dusting:** Sprinkle prime on surface of wet (damp) composition, frequently used on cut stars. (Not very effective because relatively little prime attaches to stars <5% prime.)
- **Layering:** Coat a heavy layer of prime on the surface of rolled (round) stars at completion of star making. (Quite effective because prime layer can be made thick.)
- **Slurry:** Dip items to be primed into a "bath" of prime (about the thickness of pancake syrup). This is normally followed by dusting with generous amounts of additional prime or granulated powder. (Quite effective. Often used with small components. Often used to coat fuses with prime applied from squeeze container.)

PRIME "SKIN" EFFECT

- **Problem: If primes are applied when too wet, a skin of "non-flammable" binder can form, rendering the prime almost fire proof.**
- **Mechanism of skin formation:**



Binder in Solution

Solvent Evaporates from Surface

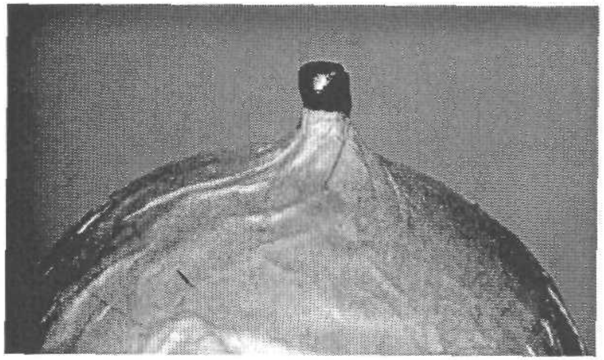
Prime

Smooth Skin, Mostly Binder

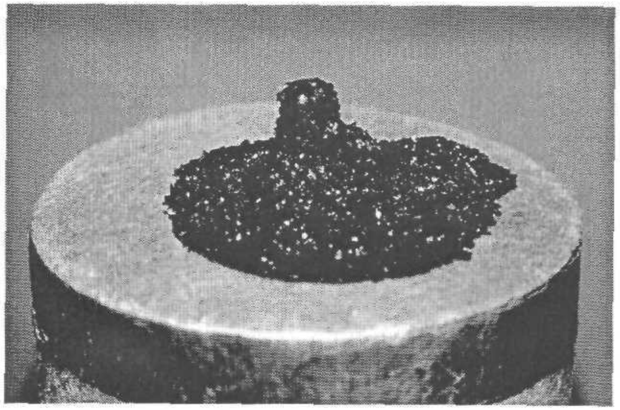
- **Solution to "skin" problem:**
  - **Minimize the amount of solvent used.**
  - **"Dust" the surface with dry prime or granular Black Powder.**
  - **Do not force dry. Force drying can cause a skin to form that acts as a vapor barrier, preventing further drying.**

PRIME APPLICATION EXAMPLES

- Example of an ineffective (hard, shiny, smooth) application of prime.

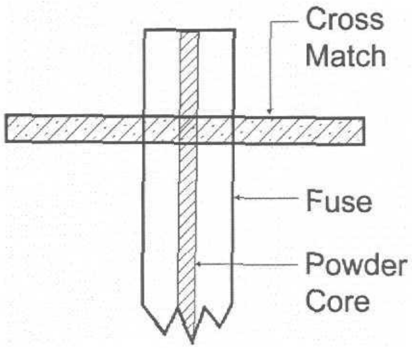


- Example of prime pressed into granulated powder with *excellent ignition properties.*

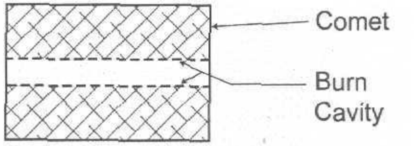


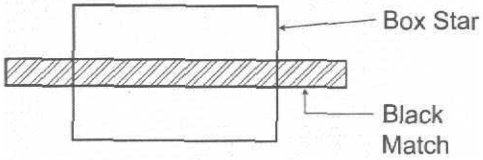
ALTERNATIVES TO PRIMING

- Cross matching.



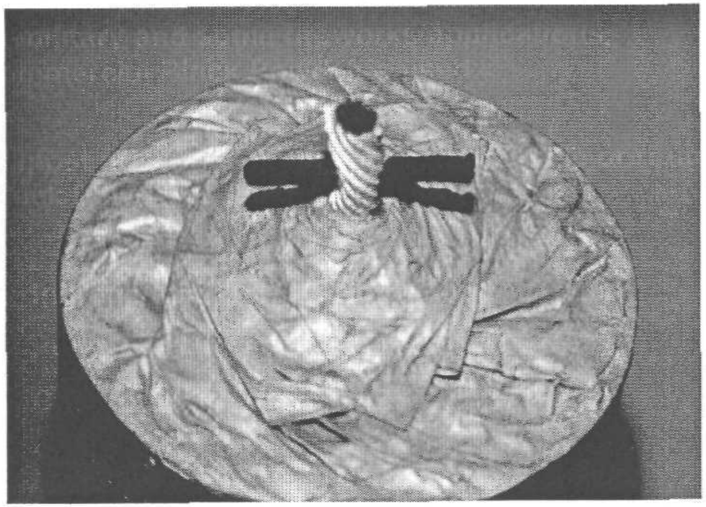
- Use an initial composition that is "prime-like".
  - For example — color-change stars with meal-powder-like comet composition as first effect.
- Use a burn cavity through the composition.





CROSS MATCH EXAMPLE

- Example of "cross matching" a Bickford style (time) fuse.



ADDITIONAL FORMULATIONS

Potassium Perchlorate Hot Prime (Jennings-White)

Potassium perchlorate	60	Comment:
Charcoal (air float)	15	Based on Kosanke's lance prime formulation.
Silicon powder	10	Both takes and gives fire with facility. No
Zirconium (60-200 mesh)	10	problem rolling on round stars using alcohol.
Accroides gum (red gum)	5	One stage prime for hard to light ammonium perchlorate stars.

Sulfurless Dark Prime (Jennings-White)

Handmade sulfurless meal powder	50	Comment:
Potassium nitrate	40	Shimizu's antimony sulfide dark prime on chlorate
Shellac	10	stars is not recommended.

Magnalium Thermite (Jennings-White)

Iron(III) oxide (red)	75	Comment:
Magnalium (20:80, 200 mesh)	25	The use of 20:80 magnalium mitigates the ignition difficulties.

First Fire (Ellern)

Silicon	25	Comment:
Red lead	25	Accepts fire readily and burns hot, producing
Titanium	25	molten material.
Iron oxide (red)	25	

Tracer Igniter (Ellern)

Magnesium (fine)	20
Barium peroxide	78
Calcium resinate	2

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SECTION 4

FACTORS AFFECTING BURN RATE

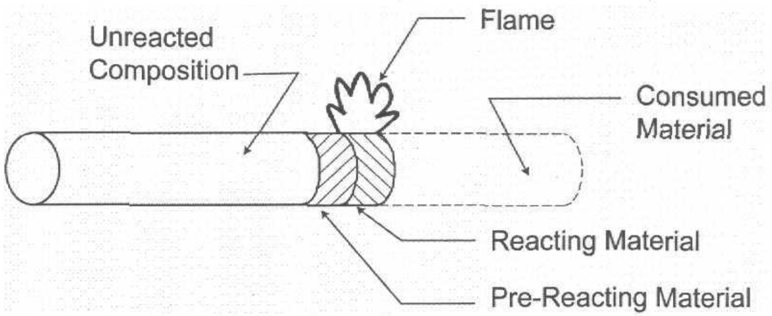
- Choice of Chemicals
- Fuel to Oxidizer Ratio
- Degree of Mixing
- Particle Size and Shape
- Additives and Catalysts
- Temperature, Pressure and Confinement
- Physical Form and Consolidation
- Geometry, Crystal and Environmental Effects

WHY DO YOU WISH TO CONTROL BURN RATE?

- Because of performance, aesthetic and safety reasons, the following are undesirable:
  - Stars (aerial flares) that burn so slow that they fall to the ground still burning.
  - Rockets that fail to lift off because of low thrust.
  - Rockets that explode because the internal pressure exceeds the motor casing strength.
  - Salutes (photo flash charges) that burn like fountains.
  - Flash powder that explodes in small quantity, even when unconfined.
  - Hand grenade delay fuse that burns faster than expected.
- The factors that affect burn rate are what can be used to control burn rate.

FACTORS AFFECTING PYROTECHNIC BURN RATE

- In essence, burn rate is determined by how quickly the pre-reacting layer of composition can be raised to its ignition temperature.



- The factors that control burn rate are those things that affect:
  - Activation energy (E_a),
  - Heat of reaction (ΔH_r), or
  - *Efficiency of thermal energy feedback (E_f).*

MANNER OF CONTROLLING BURN RATE

- Burn rate may be adjusted by:

Control Mechanism	Effect on Burn Rate
Lowering E_a	Higher burn rate
Raising ΔH_r	Higher burn rate
Increasing feedback	Higher burn rate
Raising E_a	Lower burn rate
Lowering ΔH_r	Lower burn rate
Decreasing feedback	Lower burn rate

- Those things affecting the efficiency of energy feedback are directly related to the three mechanisms for conveying thermal energy.

Transfer Mechanism	High Feedback Efficiency
Convection	Many fire paths
Radiation	Black or dark compositions
Conduction	Metal fuels and compaction

FACTORS AFFECTING BURN RATE

- There are at least 15 factors that can influence (control) burn rate.

Controlling Factor	E_a	ΔH_r	F_{fb}
Choice of fuel and oxidizer	X	X	X
Fuel to oxidizer ratio		X	
Degree of mixing		X	
Particle size	X		
Particle shape	X		
Presence of additives	X	X	X
Presence of catalysts	X		
Ambient temperature	X		
Local pressure			X
Degree of confinement			X
Physical form			X
Degree of consolidation			X
Geometry			X
Crystal effects	X		X
Environmental effects	X	X	X

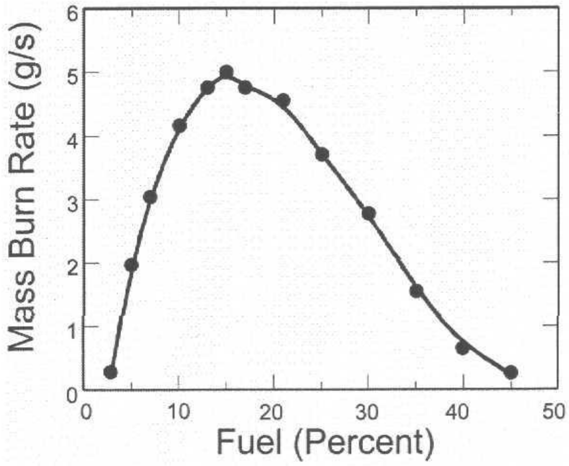
“X” Indicates major control mechanisms.

EFFECT OF CHOICE OF CHEMICALS ON BURN RATE

- The chemicals chosen can affect all three factors controlling burn rate.
  - Activation energy differences
    - = $KClO_3$ – Exothermic decomposition (low E_a).
    - = KNO_3 – Endothermic decomposition (high E_a).
  - Heat of reaction differences for combustion
    - = Al $\Delta H_r = 7.4$ kcal/g (high).
    - = S $\Delta H_r = 2.2$ kcal/g (low).
  - Energy feedback differences
    - = Metals – High thermal conductivity.
    - = Non-Metals – Low thermal conductivity.
- *For Example:*
  - $KClO_3 + Al \rightarrow$ High burn rate (flash powder).
  - $KNO_3 + S \rightarrow$ Low burn rate (barely burns).

EFFECT OF FUEL TO OXIDIZER RATIO ON BURN RATE

- **As the fuel to oxidizer ratio varies from the ideal ratio (that required for complete burning), burn rate generally decreases.**
  - **Example — Burn rates for mixtures of boron and barium chromate** [Domanico].

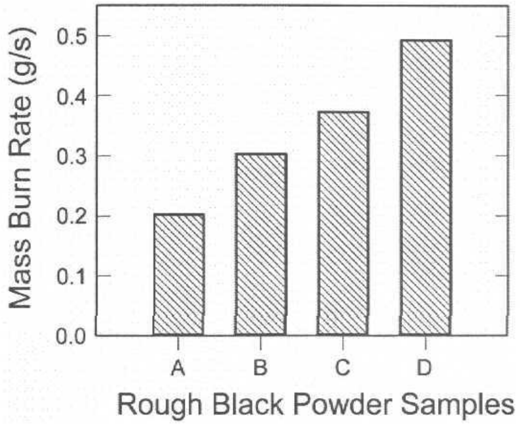


- **The burn rate decreases because the excess fuel or oxidizer fails to contribute any energy (i.e., heat of reaction is reduced). It could also be thought of as consuming energy because the excess material must be heated along with the rest of the composition.**

EFFECT OF MIXING ON BURN RATE

- **Before being well mixed, most of the material will be far from the ideal ratio, and burn rate will be quite low. As mixing continues, the burn rate increases toward its maximum value.**

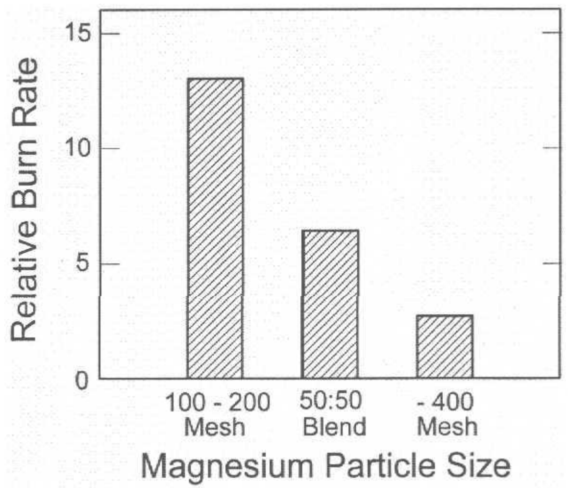
- **Incorporation — The process of bringing fuel and oxidizer into more intimate contact.**



- **Incorporation Example** [Kosanke]:
  - **A – Dry mixed several times through 60-mesh screen.**
  - **B – Wet mixed for several minutes with mortar and pestle.**
  - **C – Wet ball milled for 4 hours, dried and crushed to –100 mesh.**
  - **D – Fuels dry ball milled for 4 hours, oxidizer added and wet ball milled for 8 hours, dried and crushed to –100 mesh.**

EFFECT OF PARTICLE SIZE ON BURN RATE

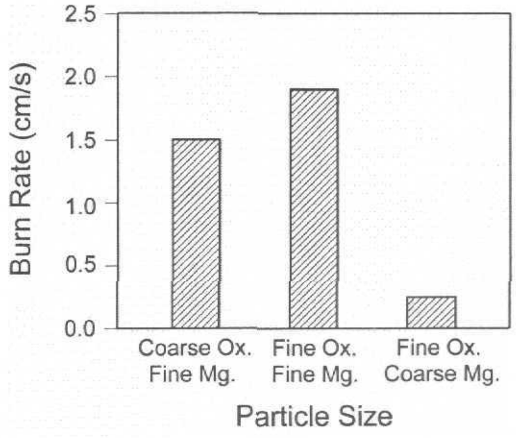
- **As particle size is reduced, burn rate increases. This is because small particles are more easily heated during the reaction (i.e., E_a is reduced). In addition, the fraction of atoms that are on the surface of particles increases as size decreases.**
- **Example — Burn time of flares made using different size magnesium particles** [Domanico].



- **This can also be thought of as the result of a particle's surface to mass ratio. Small particles, with a high surface to mass ratio, are more reactive.**

EFFECT OF PARTICLE SIZE ON BURN RATE (Continued)

- **The particle size effect is most noticeable for fuels; oxidizers usually have started to melt (or have melted) before the ignition temperature is reached.**
- **Example — Burn rates for mixtures of strontium nitrate (60%), magnesium (25%) and PVC (15%)** [Domanico].



- **Mesh range for fine magnesium was 200–325; coarse magnesium was 30–50; mesh range for fine and coarse oxidizers was not specified.**

MESH AND SIEVE SIZES

- Mesh number and particle size for standard sieves.

Mesh Number*	Space Between Wires (inches)	Space Between Wires (microns)	Typical Material
14	0.056	1400	Beach sand
28	0.028	700	
60	0.0098	250	Fine sand
100	0.0059	150	
200	0.0030	74	Portland cement
325	0.0017	44	Fine silt
400	0.0015	37	Plant pollen
(600)	0.0010	25	
(1200)	0.0005	12	Red blood cell
(2400)	0.0002	6	
(4800)	0.0001	2	Cigarette smoke

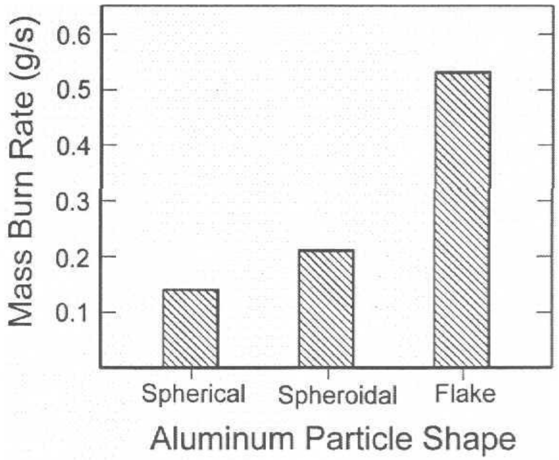
* US Standard Sieve. Mesh number is the number of standard diameter wires per inch of wire mesh.

( ) Indicates effective mesh number for sub-mesh sized particles.

EFFECT OF PARTICLE SHAPE ON BURN RATE

- Particle shape affects burn rate in much the same way as particle size. Spherical particles do not heat quickly (have a relatively low surface to mass ratio). Thus, they have a relatively high activation energy. Flakes are at the other extreme, producing compositions with the lowest activation energy.

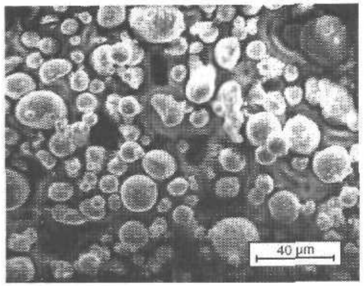
- Example — Burn rates for mixtures of potassium perchlorate (64%), ~20μ aluminum (27%) and red gum (9%) pressed into 1 cm diameter tubes [Kosanke].



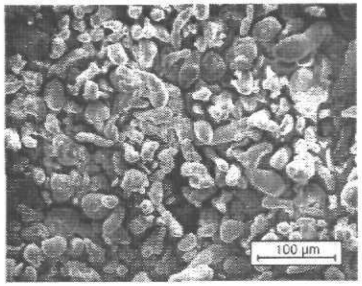
- Particle shape is most important for fuels because oxidizers usually have started melting before ignition.

ALUMINUM PARTICLE SHAPES

- When molten aluminum is sprayed into an atmosphere containing oxygen, a crust of Al_2O_3 quickly forms causing the particle to assume highly distorted shapes.

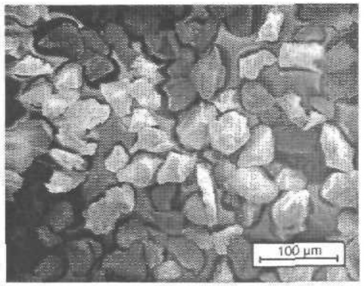


Spherical Atomized

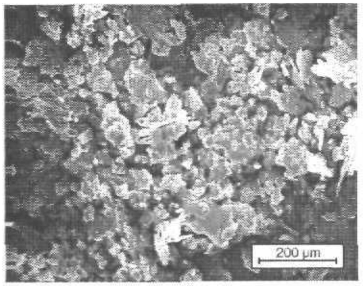


Spheroidal Atomized

- Flake aluminum is made by milling other particle shapes. The impacts during milling will cause the flakes to stick together, unless a lubricant is added.



Granular



Flake

EFFECTS OF ADDITIVES ON BURN RATE

- Pyrotechnic Additive — Material added to a composition for achieving a specific pyrotechnic effect or purpose.

- Examples:

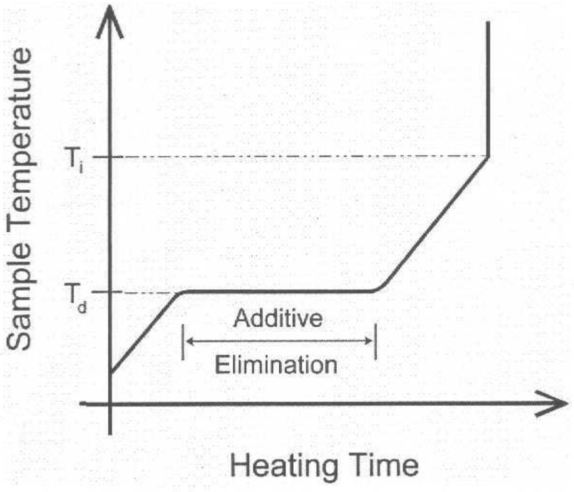
$BaCO_3$ — Acid neutralization
$NaHCO_3$ — Glitter delay
PVC — Chlorine donor
$SrSO_4$ — Color agent
Dextrin — Binder
Water — Hydration of binder
Lampblack — Infrared absorber

- Most additives lower burn rate either by increasing activation energy (E_a) or reducing heat of reaction (ΔH_r).

- However, some additives may increase burn rate, generally by raising the heat of reaction (ΔH_r) or increasing the fraction of energy fed back (F_{fb}).

SOME PYROTECHNIC ADDITIVES RAISE THE ACTIVATION ENERGY

- **Additives may consume energy (heat) in their decomposition or elimination.**

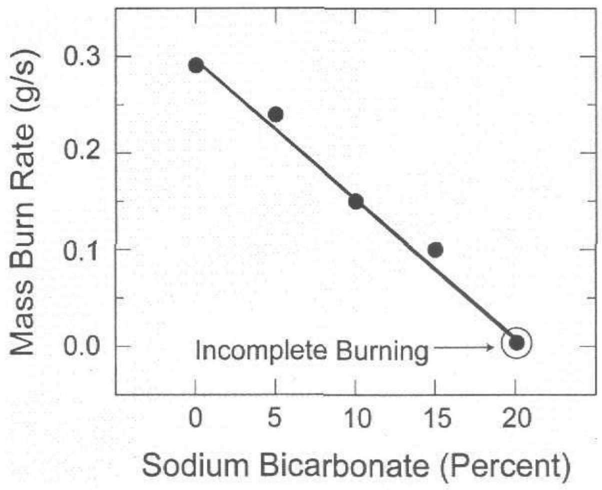


- **Consider the effect of sodium bicarbonate ($NaHCO_3$), which decomposes at 270 °C (T_d) to produce CO_2. As the pre-reacting material is heated, its temperature rises toward T_d. Upon reaching T_d, decomposition occurs consuming energy and holding the temperature at T_d. After all of the $NaHCO_3$ has decomposed, the temperature again rises toward the ignition temperature (T_i).**

DEMONSTRATION OF THE EFFECT OF SODIUM BICARBONATE ON BLACK POWDER

- **When sodium bicarbonate is present, an added period of time elapses before the Black Powder (meal) reaches its ignition temperature. This added time manifests itself as a lower burn rate.**

- **Example — Burn rate of loose (–100 mesh) rough Black Powder with added amounts of sodium bicarbonate** [Kosanke].



- **At about 20% sodium bicarbonate, burning becomes unstable and may cease altogether.**

SOME PYROTECHNIC ADDITIVES LOWER THE HEAT OF REACTION

- Additives may function as a fuel or oxidizer; however, they may produce less energy than the principal fuel or oxidizer.
- Examples:

Fuel	Purpose	Heat of Combustion (kcal/g)
C	Primary fuel	7.8
Al	Primary fuel	7.4
PVC	Color enhancer	4.4
Dextrin	Binder	4.2

- The presence of these additives lowers the overall heat of reaction for the composition, and, therefore, generally lowers the burn rate as well.

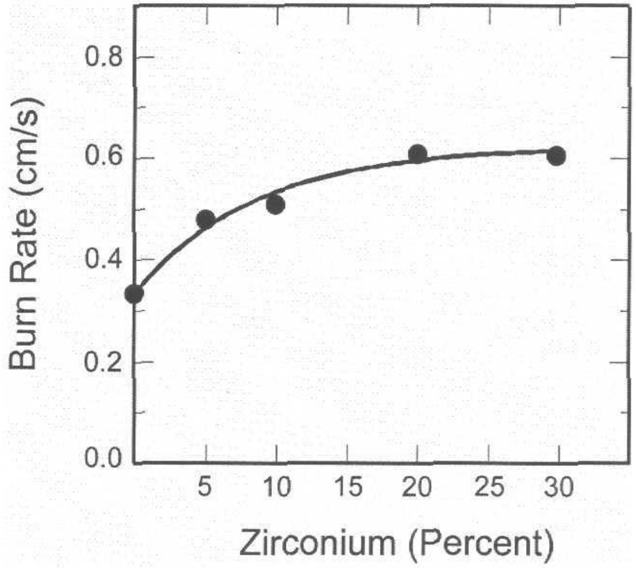
EFFECT OF BURN RATE MODIFIERS

- Burn Rate Modifier — An additive used for the primary purpose of adjusting burn rate (up or down).
- A burn rate modifier can act to reduce burn rate as described for typical additives.
- A burn rate modifier can act to increase burn rate. This will be the case if it increases the heat of reaction or if it increases the efficiency of thermal energy feedback.
- Examples:

– Zirconium powder	– Increases heat of reaction (some increase in conductive feedback efficiency).
– Lampblack	– Increases radiant energy feedback efficiency.

EXAMPLE OF AN ACCELERATING BURN RATE MODIFIER (ADDITIVE)

- In this case, the effect of adding fine zirconium to red tracer mix (R328) has the effect of increasing burn rate [Domanico].



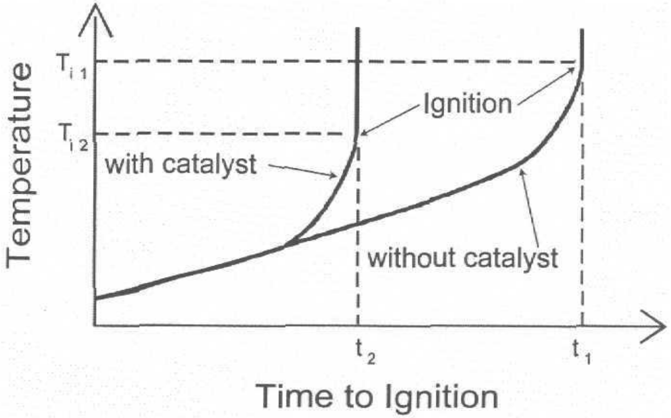
- Note that the initial addition of zirconium produces the greatest increase in burn rate (i.e., adding the first 5% zirconium produces about 50% of the total increase in burn rate).

EFFECT OF CATALYSTS ON BURN RATE

- Catalyst — A chemical (generally not consumed in the reaction) that increases the rate of the reaction. (Pyrotechnic catalysts are often consumed because of high temperatures during burning.)

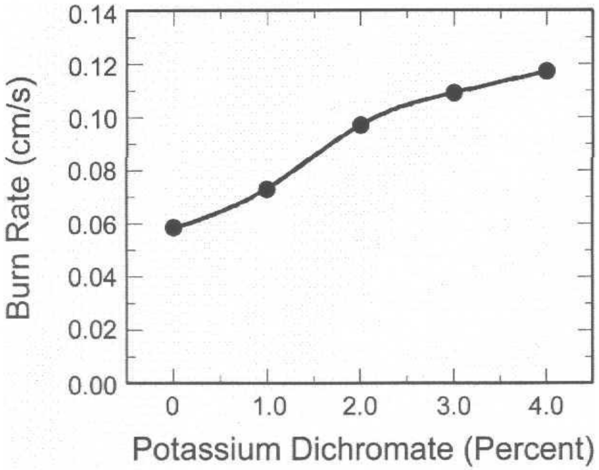
  MnO_2 — **Manganese dioxide**
  Fe_2O_3 — **Iron(III) oxide, red**
  $K_2Cr_2O_7$ — **Potassium dichromate**

- Burn catalysts often act by lowering activation energy by lowering the decomposition temperature of an oxidizer. This lowers ignition temperature and increases burn rate, because less time is required to reach the now lower ignition temperature.



EFFECT OF CATALYSTS ON BURN RATE (EXAMPLE)

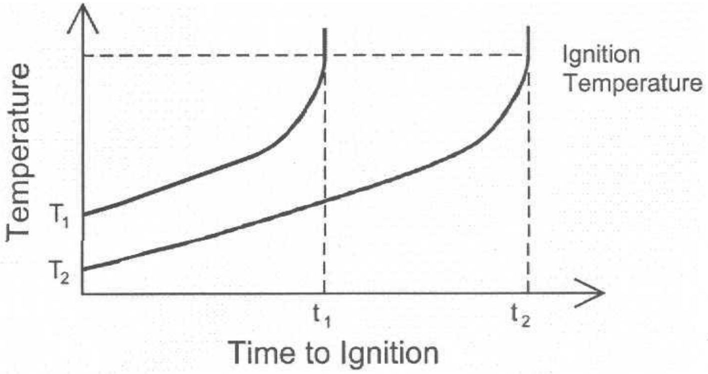
- Example:
  - Normally potassium chlorate melts at 360 °C with little decomposition. When manganese dioxide is added, the decomposition temperature is lowered by 70–100 °C [Ellern].
  - Burn rate of mixtures of potassium perchlorate and potassium dichromate (70% total) + shellac (30%) pressed into 1 cm diameter paper tubes [Kosanke].



  - Adding 4% potassium dichromate doubled burn rate.

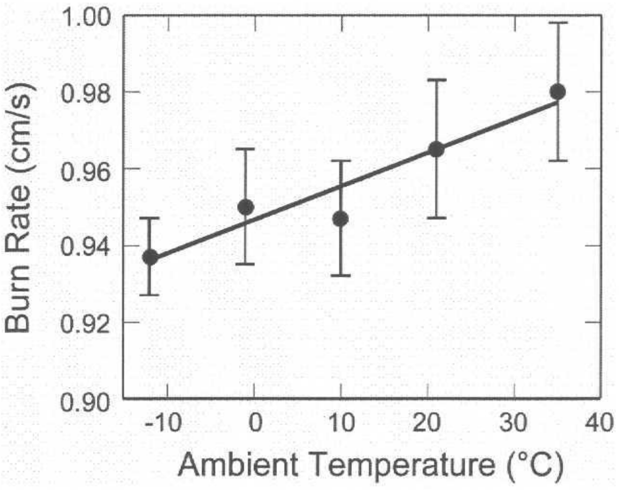
EFFECT OF TEMPERATURE ON BURN RATE

- Ambient temperature — The temperature of the surroundings; normally, also the temperature of the unreacted composition.
- As ambient temperature is raised, activation energy is lowered because less energy is needed to raise a composition to its ignition temperature. Thus the burn rate is increased because less time is required to reach the ignition temperature.



EFFECT OF TEMPERATURE ON BURN RATE (EXAMPLE)

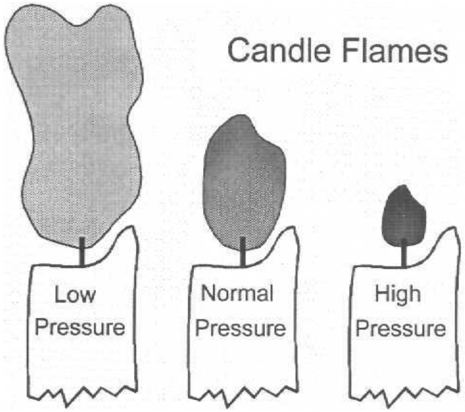
- **Samples of visco (hobby) fuse were burned at various temperatures** [Kosanke].



- **Fuse burn rate increased by about 4.5% with a temperature increase of about 45 °C (85 °F).**

EFFECT OF LOCAL PRESSURE ON BURN RATE

- **An increase in ambient pressure raises flame temperature, and the flame is held closer to the burning surface.**



- **When flames burn hotter and are held closer to the burning surface, the efficiency of energy feedback is increased, which thus increases burn rate.**

- **The extent to which pressure affects burn rate depends on the extent to which burning takes place as a gas.**
  - **Thermite — almost not affected (gasless).**
  - **Black Powder — moderately affected (40% gas).**

EFFECT OF AMBIENT PRESSURE ON FLAME

- **Typical flame photographs of NC-NG double-base propellant.**

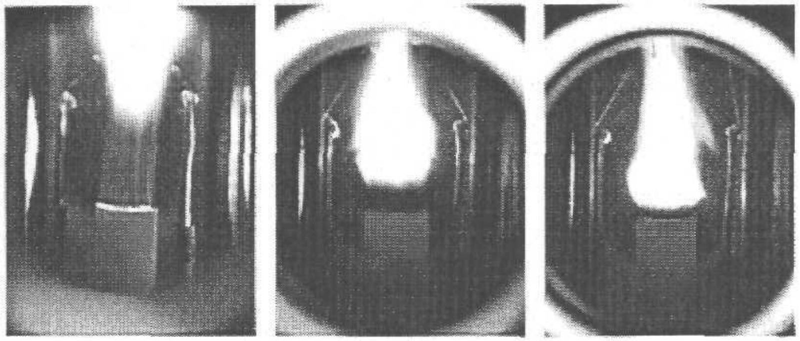
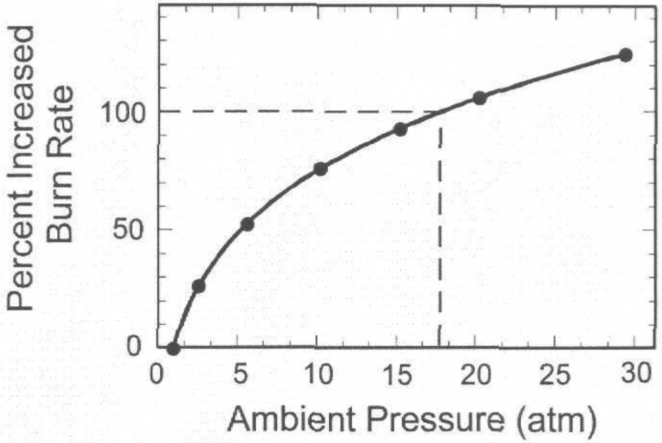


Photo from *Propellants and Explosives: Thermochemical Aspect of Combustion* By Naminosuke Kubota, Wyley-VCH (2002).

- **A is at 1.0 MPa with a burn rate of 2.2 mm/s.**
- **B is at 2.0 MPa with a burn rate of 3.1 mm/s.**
- **C is at 3.0 MPa with a burn rate of 4.0 mm/s.**

EXAMPLE OF PRESSURE EFFECT ON BURN RATE

- **The functional relationship between pressure and Black Powder burn rate is shown below** [Conkling].



- ***The general relationship between burn rate and* pressure is expressed by the burn rate (Vieille) equation:**

$$R = A P^{B}$$

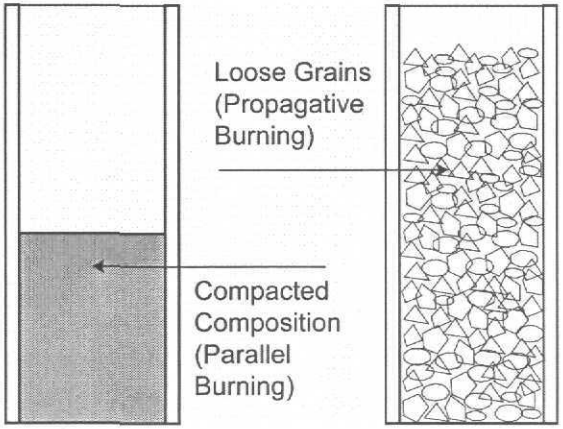
- **When the burn rate (R) is in cm/s and pressure (P) is in atmospheres, then for Black Powder, the constant A is 1.21 and B is 0.24 [Shidlovskiy].**

EFFECT OF CONFINEMENT ON BURN RATE

- When a burning pyrotechnic composition is confined, obviously pressure can increase to very high values.
- Temperatures produced when a burning composition is confined are also higher, because high temperature gases and radiant energy cannot escape.
- Increases in temperature and pressure each act to increase burn rate. Thus, confinement can greatly increase burn rate.
- Further, if the type of burning transitions from parallel to propagative burning, burn rate may increase tremendously. [Discussed later.]
- Finally, deflagration to detonation transitions may be possible. [Discussed later.]

EFFECT OF PHYSICAL FORM ON BURN RATE

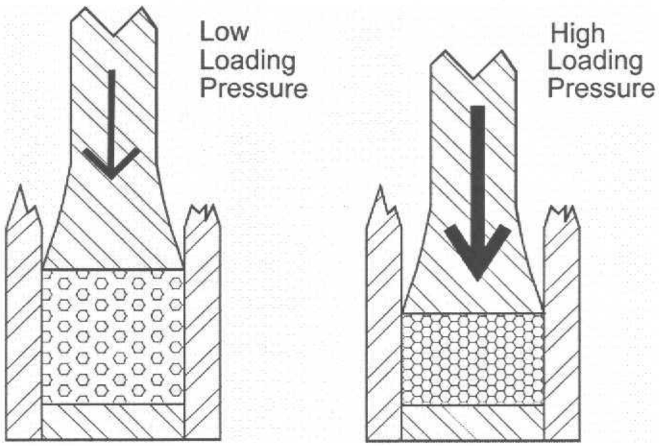
- There are two general types of pyrotechnic burning (parallel and propagative – discussed later). The same material will be consumed at a much greater rate if propagative burning occurs.
- The type of burning that occurs depends on whether gases are produced and on the physical form of the pyrotechnic material (compacted solid or loose granular).



- The burn rate of compacted Black Powder is about 0.5 cm/s. However, granular Black Powder burns at about 60 cm/s in the open [Urbanski] or at about 1000 cm/s if confined as above [Kosanke].

EFFECT OF LOADING PRESSURE ON BURN RATE

- **Loading Pressure — The pressure applied in compacting a pyrotechnic composition. Increasing loading pressure increases compaction. This increases thermal conductivity, but closes fire paths.**

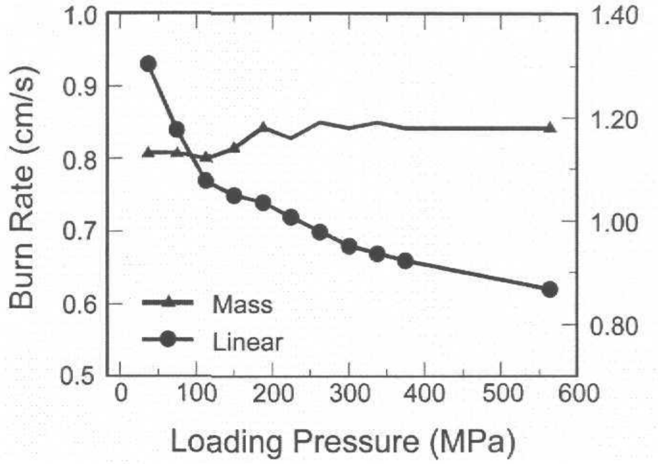


- **When no gas is produced upon burning: Increases in loading pressure increase thermal conductivity, which generally increases burn rate.**

- **When gases are produced upon burning (true for essentially all fireworks compositions): Increases in loading pressure reduce gas penetration into the unburned composition, which generally decreases burn rate.**

EFFECT OF LOADING PRESSURE ON BURN RATE (EXAMPLE)

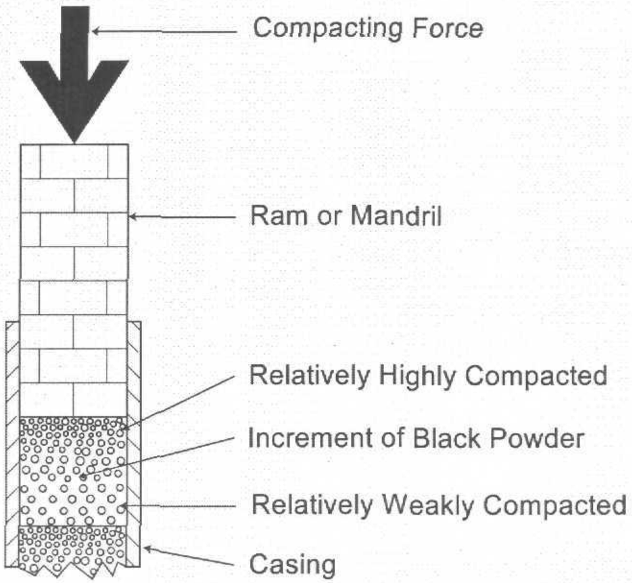
- **Samples of Pyrodex™ were burned after being compacted with various loading pressures** [Barrett].



- **Note that while linear burn rate falls significantly, mass burn rate is constant or rises slightly. This is not an uncommon result.**

LOADING PRESSURE AFFECTINGBURN RATE

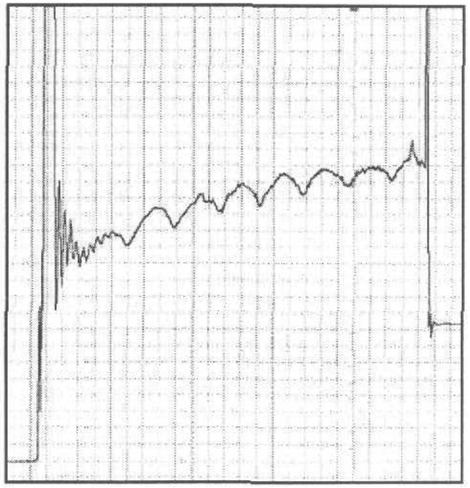
- **When increments of powder are compacted, the effective loading pressure varies with distance through the increment. The material closest to the ram is the most compacted.**



- **Because of this variation in compaction, it is generally felt that the approximate height of each increment should be not greater than the inside diameter of the tube.**

LOADING PRESSURE AFFECTING BURN RATE (Continued)

- **The thrust profile of a Black Powder rocket, displays variations corresponding to the number of increments.** [T. Dimock]

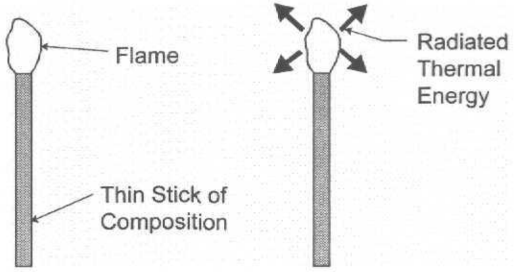


- ***All else being equal, the amount of thrust of a rocket* motor is proportional to the burn rate.**

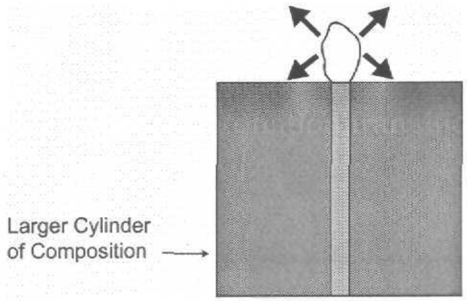
- **Thus, the observed variations in thrust likely correspond to variations in effective loading pressure or compaction within each increment.**

EFFECT OF SURFACE AREA ON BURN RATE

- As the size of the burning surface increases, burn rate generally also increases. This is because the efficiency of thermal energy feedback increases.



- With a thin stick of composition, essentially all radiant energy is lost to the surroundings (low feedback efficiency).



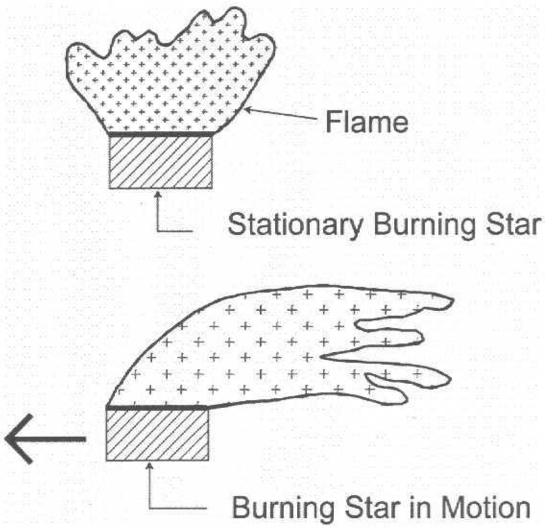
- When the stick of composition is part of a larger cylinder of composition, much of the downward directed radiation will be absorbed by other parts of the composition (higher feedback efficiency).

CRYSTAL EFFECTS ON BURN RATE

- Crystal effects are any of a collection of ways in which energy can be stored in a crystal lattice or in which crystal properties can affect burn rate.
  - The process of grinding can result in energy being stored in imperfections in the crystal structure. After grinding, there is a relaxation time during which the energy slowly drains away.
  - Impurities trapped in the crystal lattice can participate in chemical reactions or alter the physical properties of a crystal.
  - It has been suggested that piezoelectric effects could be important in transitions from deflagration to detonation. This might occur as pressure effects are converted to an electrical stimulus.
- Energy stored in crystals and the effect of many impurities is to lower the activation energy of a composition. Piezoelectric crystals could increase the efficiency of energy feedback.

ENVIRONMENTAL EFFECTS ON BURN RATE

- **Changes in ambient temperature or pressure are not what is meant by environmental effects. A common environmental effect is wind, generally produced by having a burning pyrotechnic item propelled through the air at high speed.**



- **The flame produced tends to fall behind resulting in less efficient energy feed back.**

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SECTION 5

ASPECTS OF PYROTECHNIC BURNING

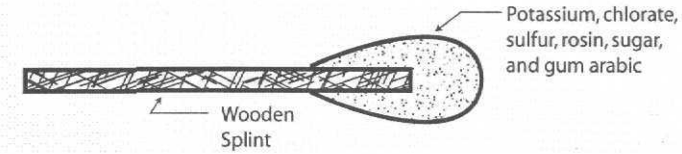
- Igniters
- Pyrotechnic Delays
- Parallel vs. Propagative Burning
- Black Match / Quick Match Mechanism
- Rocket Performance / Malfunctions
- Burning / Deflagration / Detonation

PYROTECHNIC IGNITERS

- Pyrotechnic igniters typically convert one form of energy (friction, impact, electrical) into sufficient thermal energy to reliably cause the ignition of something else.
  - Friction devices include:
    - = Common safety match
    - = Fusee igniter
    - = Pull wire igniter
  - Impact devices include:
    - = Small arms primer
    - = Stab igniter
  - Electric (thermal) devices include:
    - = Electric match
    - = Squib and detonator
    - = Semiconductor bridge igniter
- Of necessity, most pyrotechnic igniter compositions are relatively sensitive to the various ignition stimuli.

MATCHES

- **"French fire-matches" (ca. 1805) utilized a pyrotechnic composition ignited by dipping into sulfuric acid.** [Finch]



$$2\,KClO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2\,HClO_3{}^*$$

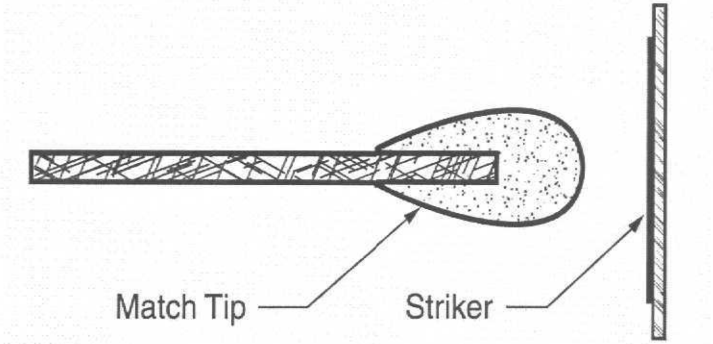
*** Causes spontaneous ignition of organic fuels.**

- **Early friction matches (ca. 1830) look much like that above and were ignited by pulling the match from between a fold of sand paper.** [Finch]

Ingredient	English	French
Potassium chlorate	28	41
Antimony sulfide	25	18
Sulfur	6	12
Ferric oxide	6	4
Gum arabic	35	25

MATCHES (Continued)

- **Safety matches appeared by about 1900 and involved two compositions (match tip and striker).** [Finch]

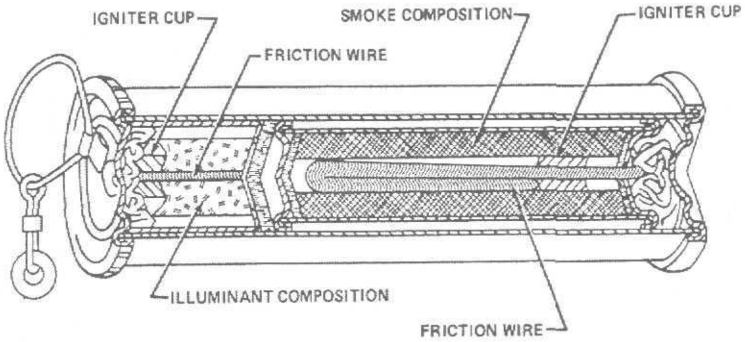


Ingredient	Tip	Striker
Potassium chlorate	56	—
Potassium dichromate	2	—
Manganese dioxide	3	39
Sulfur	8	—
Red phosphorus	—	46
Iron oxide	8	2
Ground glass	16	8
Animal glue	6	—
Gum arabic	1	5

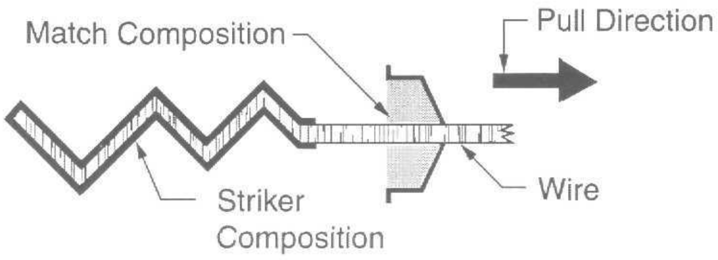
- **Most refinements in match making have been in the area of binders.**

PULL WIRE IGNITER

- Pull wire igniters are used in many small signaling devices. Ignition is accomplished using friction between a striker composition coated on a wire and a match composition in a small cup.

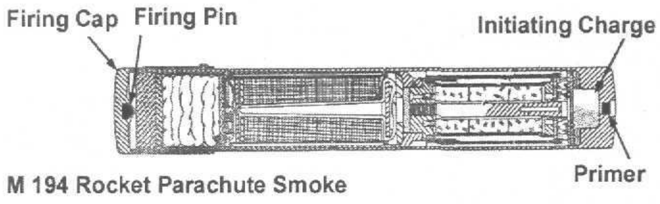


MK-13 Combination Smoke/Illumination Signal

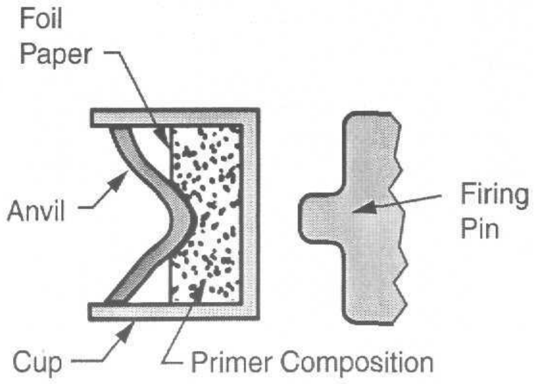


PERCUSSION PRIMER

- Percussion primers are the most commonly used ignition device. They are used in small arms cartridges and on many signaling devices.



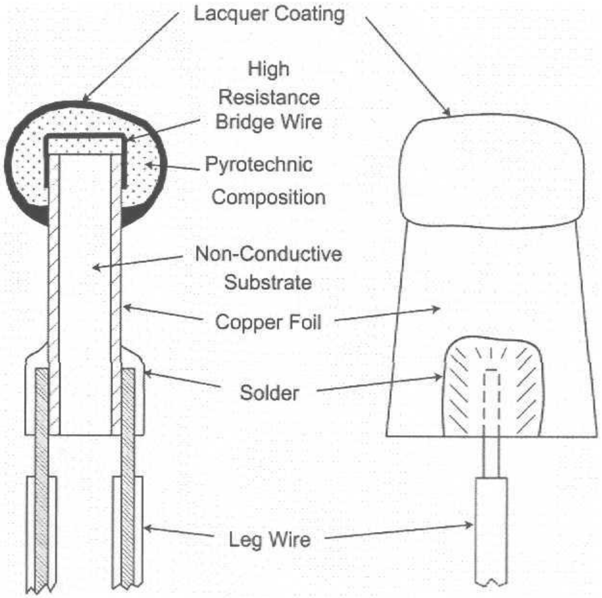
M 194 Rocket Parachute Smoke



- See formulations at end of module.

ELECTRIC MATCH (IGNITER)

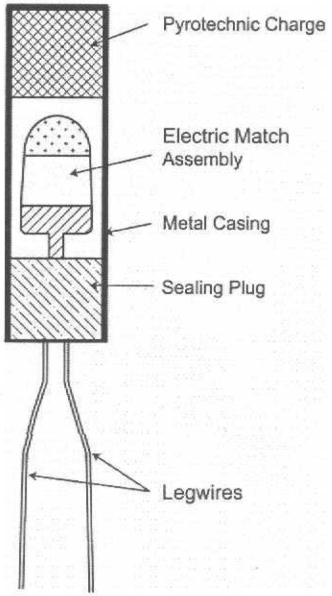
- An electric match consists of a high resistance bridge wire surrounded by a heat sensitive pyrotechnic composition. When an electric current is applied through the leg wires, the bridge wire heats up and ignites the pyrotechnic composition. This produces a small burst of fire, not unlike that from a safety match.



- Formulations are given at the end of this section.

ELECTRIC SQUIB

- A squib contains an electric match plus a base charge, not unlike a detonator (blasting cap). However, a squib contains a pyrotechnic base charge, whereas a detonator contains a high explosive base charge.



- Because of the pyrotechnic base charge, squibs produce a far greater output than an electric match. There also may be a hole in the metal casing used to direct the flame produced.

PYROTECHNIC DELAYS

- Often a time interval is needed between the initiation and functioning of a pyrotechnic device. “Delays” are used for this purpose.

- In fireworks a time interval is required between the firing of an aerial shell from its mortar and its bursting.

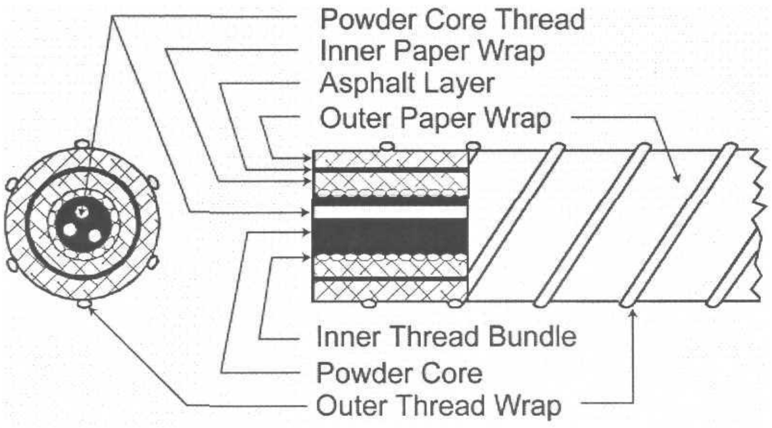
Shell Size		Approximate Delay Time
(in).	(mm)	(seconds)
3	(75)	3
4	(100)	3.5
5	(125)	4
6	(150)	5
8	(200)	6
10	(250)	6.5
12	(300)	7

- In fireworks and some military applications this is provided using Black Powder time fuse cut to various lengths.

TIME FUSE

- Commonly, in fireworks and in some military applications, delays are provided using a Black Powder time fuse.

- This “Bickford” style fuse is an internally burning fuse, generally about 1/4-inch (5 mm) in diameter. It has an ample powder core and burns about 1/3-inch per second (8 mm/s). This fuse is somewhat water resistant.



- The amount of time delay is adjusted by cutting the fuse to various lengths.

MILITARY DELAYS

- In many military applications delays ranging over a greater time span are needed. Also space may be a problem. Thus compositions with a wide range of burn rates are needed.

	Burn Rate	
Delay Columns	(in./sec)	(cm/sec)
Very fast	10	25
Fast	1	2.5
Intermediate	0.2	0.5
Slow	0.1	0.25
Very slow	0.03	0.08

- In many applications gas production is a problem. Gasless compositions are often of the Goldschmidt (thermite) type:

$$2\ \mathrm{Si} + \mathrm{Pb_3O_4} \rightarrow 2\ \mathrm{SiO_2} + 3\ \mathrm{Pb} + \text{heat}$$

CONTROLLING DELAY TIME

- The length of the delay column can be adjusted to control total burn time.
- However, for a greater range of times, the composition can be adjusted using the factors affecting burn rate discussed in the previous section.

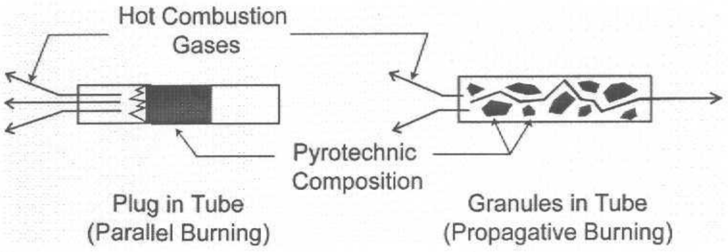
Ingredient [Ellern]	Percentage of Ingredient					
Tungsten (7–10 μ)	27	33	49	63	80	58*
Barium chromate	58	52	41	22	12	32
Potassium perchlorate	10	10	5	5	5	5
Diatomaceous earth	5	5	5	10	3	5
Burn time (sec/in.)	40	29	10	3.5	1.5	1.0

* Particle size reduced to about 2μ.

- Main factors controlling burn rate:
  - Fuel / oxidizer ratio.
  - Thermal conductivity.
  - Particle size.

TYPES OF PYROTECHNIC BURNING

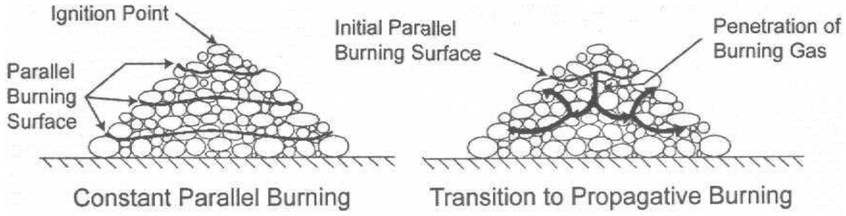
- There are two basic types of pyrotechnic burning:
  - **Parallel Burning** — Like the model of burning already discussed. Burning occurs layer by "parallel" layer until all material is consumed.



  - **Propagative Burning** — Each individual granule experiences parallel burning, but, because of penetration of hot combustion gases along "fire paths", the burning "propagates" rapidly throughout the entire mass of composition.
- The rate of propagative burning can be a 1000 times greater than parallel burning for the same pyrotechnic composition.

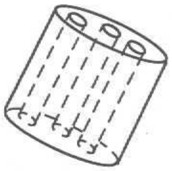
PREDICTING BURN TYPE

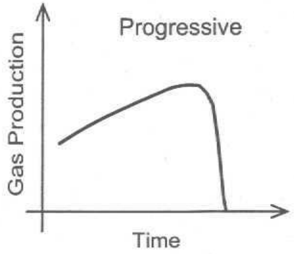
- Solidly compacted pyrotechnic compositions can generally be expected to exhibit parallel burning and to burn in a relatively mild fashion.
- Granular pyrotechnic compositions (where each grain contains fuel and oxidizer) may begin with parallel burning, but almost instantly change to propagative burning, and remain propagative until all is consumed. There is potential for this burning to be explosive (a deflagration).
- The burning of loose, fine-grained pyrotechnic powders is generally considered to be the most dangerous because the burn type is not predictable. It will begin as parallel burning, but at any instant it can change to propagative burning, with significant potential for explosion.



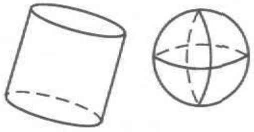
ADDITIONAL TERMS FOR PROPELLANTS

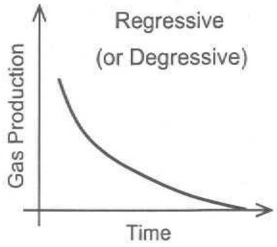
- **Propellant burning is often described with terms that can be confused with the two burn types.**
  - **Progressive Burning — The configuration of propellant grains is such that the rate of gas production increases over the burning period.**


Cylinder with Multiple Holes



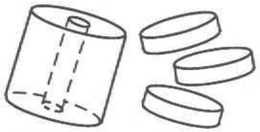
  - **Regressive (or Degressive) Burning — The configuration of propellant grains is such that the rate of gas production decreases over the period of burning.**

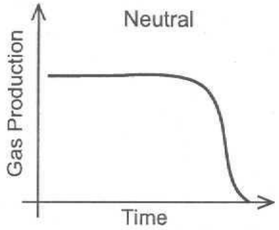

Cylinder Spheroid



ADDITIONAL TERMS FOR PROPELLANTS (Cont.)

- **Terminology (continued):**
  - **Neutral Burning — The configuration of the propellant grain is such that the rate of gas production is nearly constant over the period of burning.**


Cylinder with Hole Thin Disks



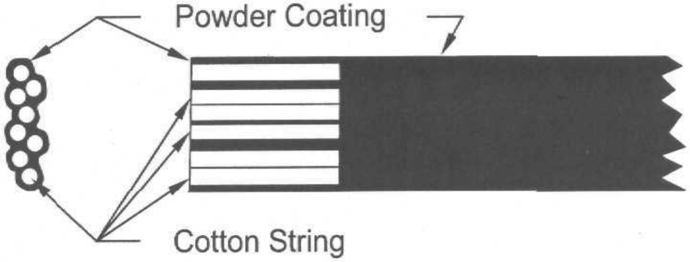
- **Erosive Burning — A type of burning in which the "normal" burn rate is augmented or increased by high gas velocity past the burning surface. Erosive burning will occur along the walls of a hole through a propellant grain.**

BLACK MATCH AND QUICK MATCH

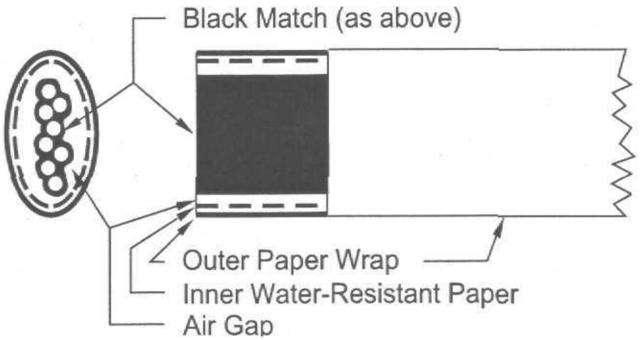
BLACK / QUICK MATCH EXAMPLE

BLACK MATCH AND QUICK MATCH

- **Black Match — A simple fuse made by coating a layer of Black Powder (with binder) on a collection of cotton strings. Black match burns about 1 in./sec (2 cm/s).**

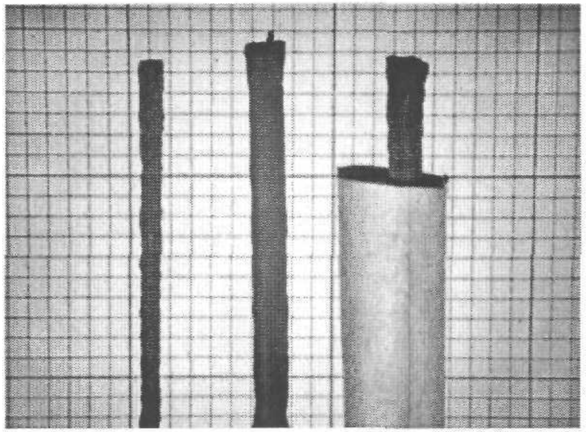


- **Quick Match — A fast burning fuse made by loosely enclosing black match in a wrap of paper or other material. Quick match burns about 10 ft/sec (3 m/s).**



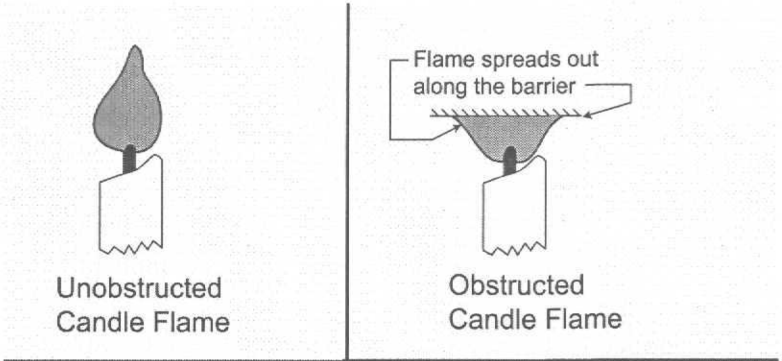
BLACK / QUICK MATCH EXAMPLE

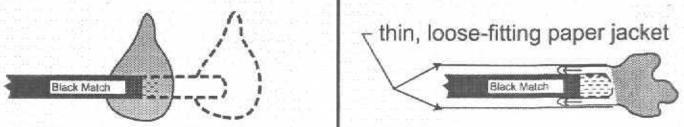
- **Example of two thicknesses of black match made with different numbers of cotton strings; also one example of quick match.**



BLACK MATCH AND QUICK MATCH BURNING

- A candle flame can be used to explain the high burn rate of quick match. In effect, black match exhibits parallel burning, whereas quick match burns propagatively.





"Black Match"

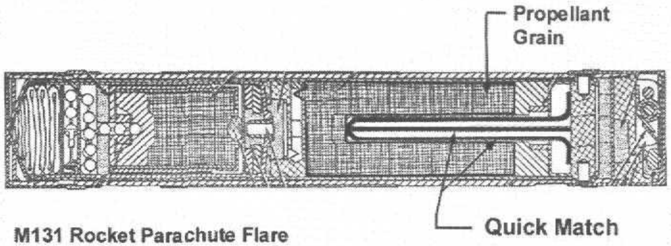
Black match exhibits essentially "parallel" burning at about 1 inch per second (except for sparks jumping ahead).

"Quick Match"

Flame spreads along inside of the paper jacket, rapidly igniting more and more black match. Quick match burns "propagatively" at 10 - 20 feet/second, about 200 times faster than black match.

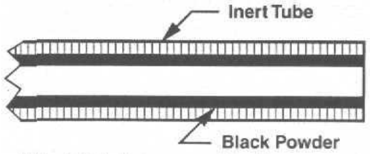
OTHER "QUICK MATCHES"

- The quick match function (propagative burning) can be accomplished without using a surrounding sheath, if that is provided by some other means.
  - Positioning black match strands in the core of a rocket produces near instantaneous ignition along the length of the core.



M131 Rocket Parachute Flare

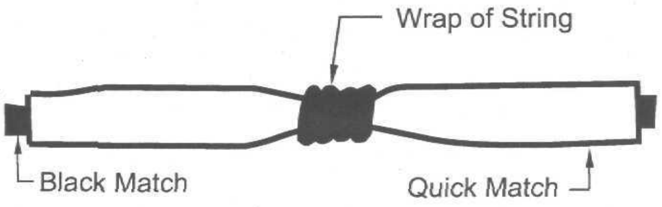
  - Coating the walls of a small diameter tube with fine grained Black Powder produces an extremely rapid burning device, "Flash Tube".

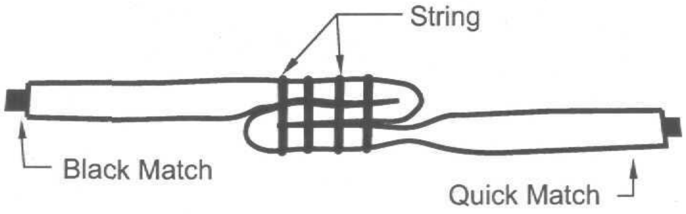


"Flash Tube"

METHODS OF SLOWING QUICK MATCH

- In fireworks, to control the rate at which finale shells fire, it is sometimes necessary to slow the burn rate of quick match.
- As a rough guide, each time a string is tied tightly around a piece of quick match, a ¼ to ½ second delay will be introduced when it burns.
- Larger delays can be achieved by tightly wrapping string around quick match, or by tying string around quick match folded in an "S" pattern.





COMPARISON OF METHODS TO SLOW QUICK MATCH BURNING

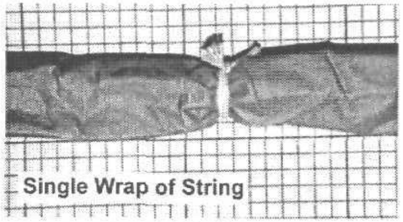
- Burn times were measured for 16 inch (40 cm) lengths of quick match using various methods of slowing. The quick match had been stored at 75 °F (24 °C) and 35% relative humidity for a month.
- Results (average of three trials each):

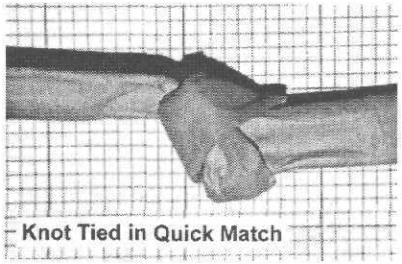
Method	Burn Time (1/60 sec.)	Slowing (Seconds)
None	19	– 0 –
String tie	33	0.2
Knot (a)	44	0.4
Cable tie (b)	47	0.5
"S" tie	48	0.5
½" string wrap	65	0.8

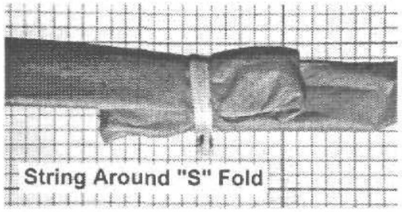
(a) A simple knot tied in the quick match itself.
(b) A 1/8"-wide plastic cable tie around the quick match.

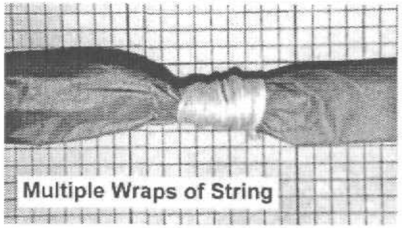
- Had the quick match been stored at a higher humidity, it would have burned slightly slower and the added delays would have been longer.

EXAMPLES OF QUICK MATCH SLOWING METHODS


Single Wrap of String


Knot Tied in Quick Match


String Around "S" Fold


Multiple Wraps of String

ROCKET PERFORMANCE

- Thrust — The propulsive force produced by a rocket motor. For a rocket to fly, thrust must exceed the total weight of the rocket (motor plus payload).

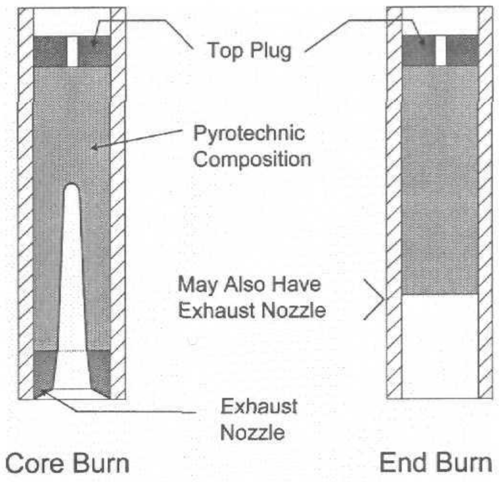
- The amount of thrust is determined by:
  - Burn rate — particle size,
    — fuel/oxidizer ratio,
    — composition,
    — etc.
  - Surface area — core diameter,
    — core length, and
    — core shape.

- When functioning, the internal pressure must not exceed the yield strength of the rocket casing. If it does, there will be a catastrophic failure of the motor.

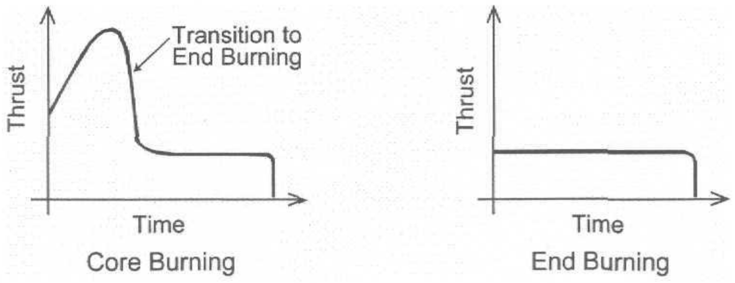
ROCKET CASE FAILURE MECHANISM

BASIC ROCKET MOTOR TYPES

- **There are two basic types of pyrotechnic rocket motors: core burning and end burning.**



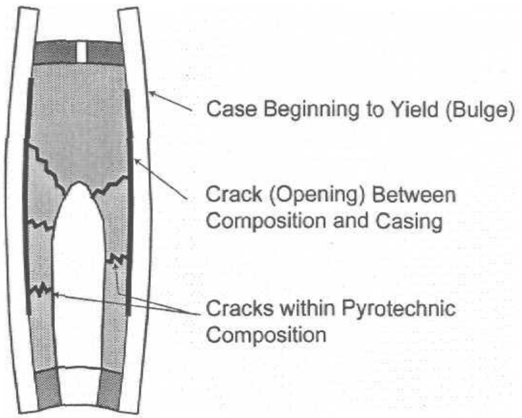
- **Thrust profiles of these motors are quite different.**



- **Most rockets are core burning because they produce more thrust.**

ROCKET CASE FAILURE MECHANISM

- **One possible mechanism for rocket motor failure.**



Initial parallel burning of composition.

High pressure causes case to bulge.

Cracks open in the pyrotechnic composition and between the composition and the casing.

Burning becomes propagative along cracks, greatly increasing the burning surface.

Pressure rises to much higher levels.

Casing ruptures catastrophically (rocket motor explodes).

ROCKET FORMULATIONS

- In model rocketry and fireworks, most rocket motors use Black Powder or compositions similar to Black Powder. Generally fireworks rockets produce a trail of sparks, which result from the addition of large charcoal or metal particles.
  - Fireworks Compositions:

Ingredient	Small Motor	Large Motor	Silver Sparks
Potassium nitrate	61	58	68
Charcoal (air float)	30	—	13
Charcoal (80 mesh)	—	33	—
Sulfur	9	9	9
Titanium (20 mesh)	—	—	10

- In military and high power sport rocketry, most motors use composite propellants.
  - Composite Compositions:

Ingredient	Percent by Weight
Ammonium perchlorate	70
Aluminum (200 mesh)	16
HTPB	14

HTPB = Hydroxy-terminated polybutadiene.

CLASSES OF COMBUSTION REACTIONS

- Combustion can be roughly divided into 3 classes:
  - Burning, Deflagration, and Detonation

Combustion Class	Burn Rate Measured in	Typical Examples
Burning	inches/minute (mm/sec)	Wood burning Safety match comp. Most fireworks comps. Unconfined Black Powder Rocket propellants
Deflagration	feet/second (m/sec)	Confined Black Powder Explosive fireworks comps. Most explosive mixtures
Detonation	miles/second (km/sec)	Dynamite Primary explosives Many explosive molecules

BURNING, DEFLAGRATION, AND DETONATION

- Burning is not well defined; it is a relatively low rate combustion reaction that "looks like burning". (There is flame production but no pressure effects.)
- Deflagration is at least mildly explosive burning, but it falls short of meeting the technical requirements for a detonation.
  - For deflagration, the linear rate of reaction is subsonic in the explosive.
- Detonation must fulfill the following relationship.

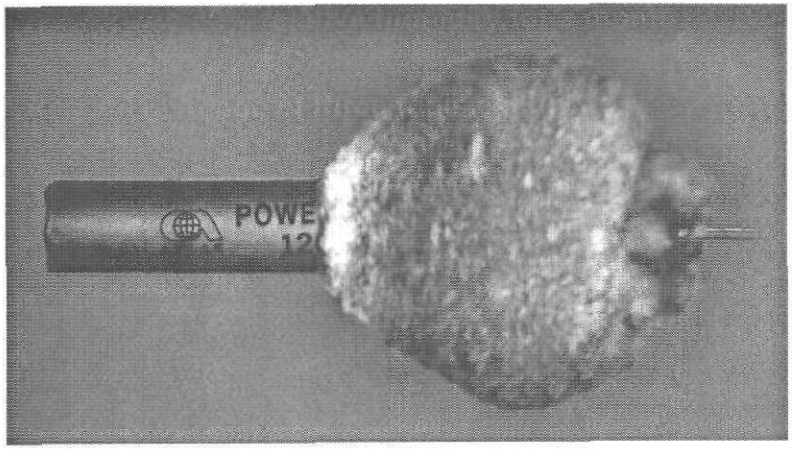
$$P_{CJ} = \rho_0 u_1 D$$

where P_{CJ} = detonation pressure
ρ_0 = density of unreacted explosive
u_1 = particle velocity
D = linear reaction rate

  - For detonation, the linear rate of reaction is supersonic in the explosive.

DETONATION EXAMPLE

- Because the reaction is propagating faster than the speed of sound in the explosive, the material to the left of the reaction zone is completely undisturbed.



(Photo Courtesy of Atlas Powder Company)

APPROXIMATE RANGES OF PARAMETERS FOR CLASSES OF PYROTECHNIC COMBUSTION

- It is not possible to set precise limits on the values of parameters for the three classes of pyrotechnic combustion. However, approximate ranges are given below.

Parameter	Burning	Deflagration	Detonation
Burn rate (m/sec)	10^{-3} – 10 << sonic	10 – 2,000 < sonic	1,500 – 10,000 > sonic
Temperature (°C)	300 – 3,500	1,500 – 4,000	2,000 – 4,000
Unconfined pressure (atm)	1	$1 - 10^2$	$1\times10^4 - 5\times10^5$
Reaction time (sec)	$1 - 10^{-3}$	$10^{-2} - 10^{-4}$	$10^{-6} - 10^{-9}$
Propagation mechanism	Thermal	Thermal and compression	Shock wave compression
Particle motion	Reverse	Primarily reverse	Primarily forward

DETONATING EXPLOSIVES — COMMONLY CALLED HIGH EXPLOSIVES (HIGH VELOCITY EXPLOSIVES)

- The three sub-classes of detonating explosives are:
  - Primary (Initiating) Explosives — can easily be initiated by thermal and mechanical energy. Examples:

    Lead azide — $Pb(N_3)_2$

    Silver fulminate — Ag(CNO)

    Lead styphnate — $Pb(C_6H_3N_3O_9)$

  - Secondary Explosives — require a detonator for initiation. Examples:

    TNT — Trinitrotoluene

    PETN — Pentaerythritol tetranitrate

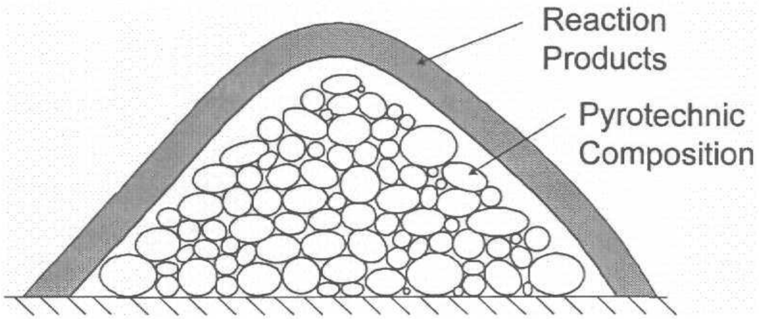
    NG — Nitroglycerin

  - Blasting Agents — require a high explosive booster for initiation. Example:

    ANFO — Ammonium nitrate/fuel oil

INERTIALLY CONFINED DEFLAGRATIONS

- **Generally, deflagrations are the result of externally supplied confinement. However, it is possible for the pyrotechnic material itself to provide sufficient confinement to produce a deflagration.**



- **Momentary confinement, caused by inertial effects of the composition and reaction products, can accelerate the burn rate to produce a deflagration (explosion).**

- **Critical Mass — The minimum amount of composition needed to cause an inertially confined deflagration. Granular Black Powder is thought to have a critical mass of about 500 pounds. Some flash powders may require only a few grams.**

ADDITIONAL FORMULATIONS:

Percussion primers [Ellern]

Ingredient	7	8	9	10	11
Lead styphnate	—	—	—	—	35.0
Basic lead styphnate	—	53	—	60	—
Tetracene	—	5	—	5	3.1
Potassium chlorate	37.0	—	53	—	—
Barium nitrate	8.7	22	—	25	31.0
Antimony sulfide	—	10	17	10	10.3
Lead thiocyanate	38.1	—	25	—	—
Powdered glass	10.5	—	—	—	—
Powdered aluminum	—	10	—	—	—
Powdered zirconium	—	—	—	—	10.3
Lead dioxide	—	—	—	—	10.3
Trinitrotoluene	5.7	—	5	—	—

Electric primer (matches) [Ellern]

Ingredient	12	13	14	15
Potassium chlorate	8.5	55	25	60
Lead mononitro resorcinate	76.5	—	—	—
Nitrocellulose, dry base	15.0	—	—	—
Lead thiocyanate	—	45	—	—
Diazodinitrophenol	—	—	75	20
Charcoal	—	—	—	15
Nitro starch	—	—	—	5

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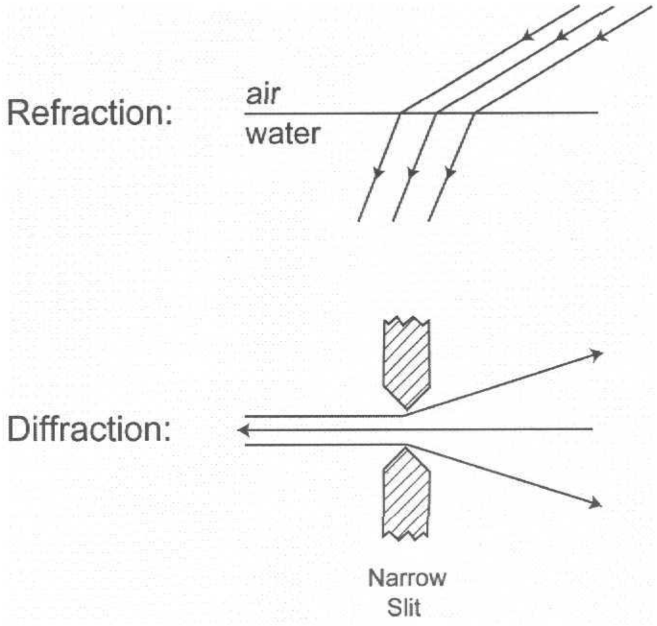
SECTION 6

PHYSICAL BASIS FOR COLORED LIGHT PRODUCTION

- Nature of Light
- Basic Quantum Theory
- Line, Band and Continuous Emissions
- Chromaticity Diagram
- Classical Color Theory
- Color Theory Applied

WAVE NATURE OF LIGHT

- Light travels from place to place as though it were a wave phenomenon (i.e., as though it were a continuous propagating phenomenon).
- Thus, light exhibits wave effects such as:



PARTICLE NATURE OF LIGHT

- **Light is emitted and absorbed as though it were a particle phenomenon (i.e., as though it were individual entities localized in space).**

- **Light particles are called *photons*, which can be thought of as being individual packets of wave energy (i.e., light has both wave and particle characteristics).**

- **The energy (E) carried by photons is proportional to their frequency (ν), or inversely proportional to their wavelength (λ):**

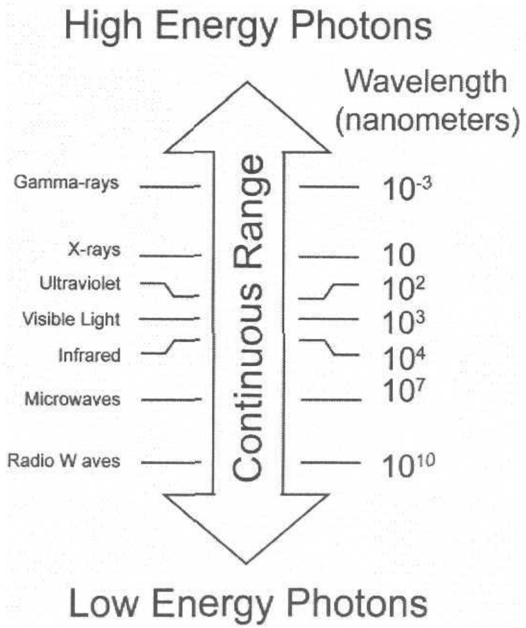
$$E = h\nu = hc/\lambda$$

where, h is a constant of proportionality (Planck's constant = 6.63×10^{-34} Js), and

c is the speed of light.

ELECTROMAGNETIC SPECTRUM

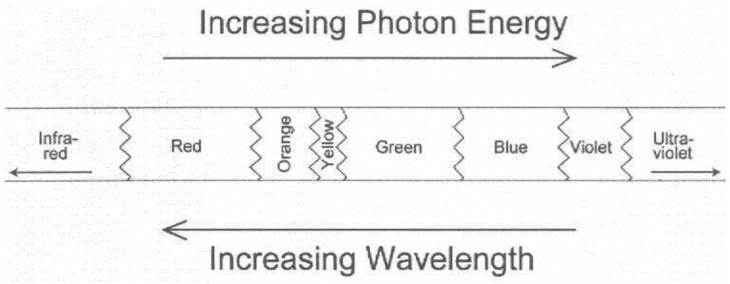
- **There is a continuous range of possible photon energies (thus there is also a continuous range of possible wavelengths and frequencies).**



- **Light — Photons with energies to which our eyes respond, plus those with slightly more energy (ultraviolet) and slightly less energy (infrared).**

VISIBLE LIGHT SPECTRUM

- **Visible light will appear different color, depending on the wavelength (energy) of the photons. The colors range from red (longest wavelength, lowest energy) to violet (shortest wavelength, highest energy).**



- **Invisible light (infrared and ultraviolet) have energies and wavelengths beyond the limits of those detected by our eyes.**

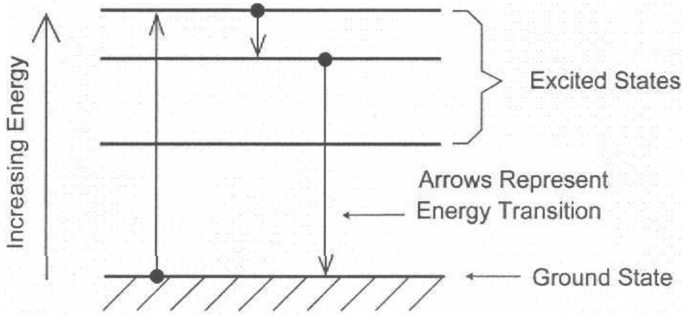
- **Wavelength Ranges for the Spectral Colors.**

Color	Approximate Wavelength (nm)
Red	700 to 610
Orange	610 to 590
Yellow	590 to 570
Green	570 to 490
Blue	490 to 450
Violet	450 to 400

QUANTUM THEORY

- **Quantum Theory — The basis for understanding atoms and molecules and the production of light.**

- **Basic tenets:**
  - **All bound systems are quantized (i.e., can only exist in certain allowed energy states).**
  - **Changes in system energy can only occur as a result of transitions between allowed energy states.**

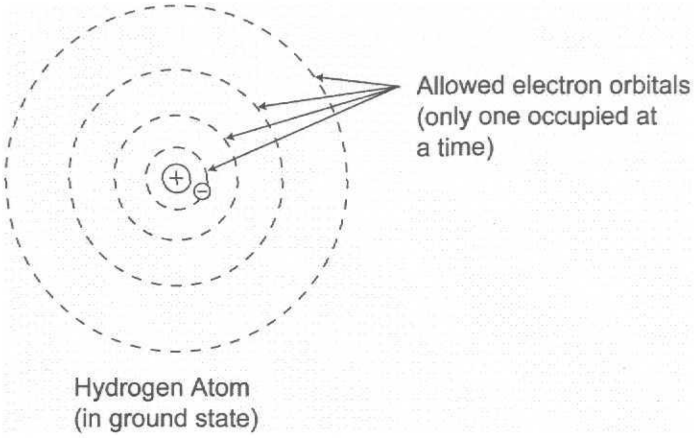


Energy Level Diagram

- **Visible light producing transitions are electron transitions in atoms and molecules.**

ATOMIC QUANTUM THEORY (HYDROGEN ATOM)

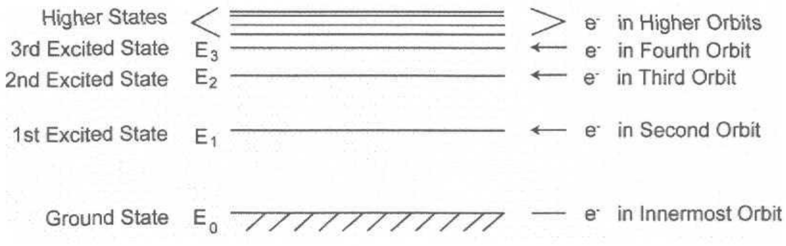
- **Atoms with their orbiting electrons are bound systems. Thus, atoms are quantized and may only exist in certain allowed energy states.**



Allowed electron orbitals (only one occupied at a time)

Hydrogen Atom (in ground state)

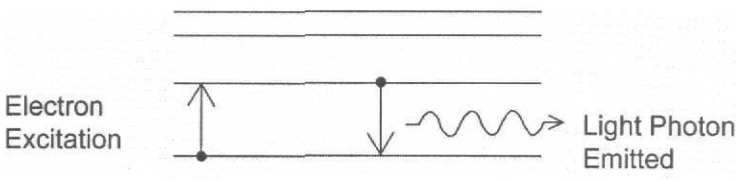
- **Energy level diagram for hydrogen atoms. (All hydrogen atoms have the same allowed energies).**



Higher States		e^- in Higher Orbits
3rd Excited State	E_3	e^- in Fourth Orbit
2nd Excited State	E_2	e^- in Third Orbit
1st Excited State	E_1	e^- in Second Orbit
Ground State	E_0	e^- in Innermost Orbit

ENERGY TRANSITIONS AND PHOTON EMISSION

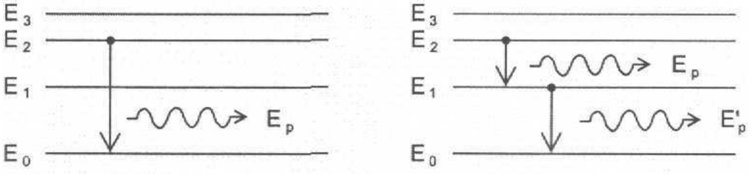
- **Photons can be produced when an electron moves from a higher to a lower energy state.**



Electron Excitation

Light Photon Emitted

- **The energy of the emitted photon (E_p) is equal to the exact energy difference between the initial and final energy levels of the transition.**



$E_p = E_2 - E_0$

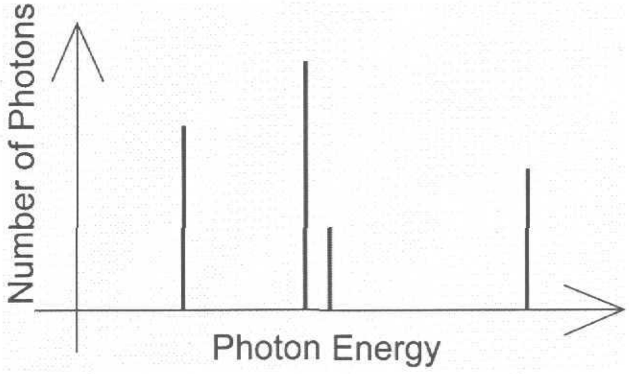
$E_p = E_2 - E_1$ and

$E'_p = E_1 - E_0$

- **Thus the color of emitted light depends on the difference between the energy states.**

ATOMIC LINE SPECTRA

- Atomic “line” spectra are produced because:
  - An atom can only exist in certain allowed energy states, each with precise energies;
  - Only transitions between these allowed electron energy states are possible.
  - Thus, the energies of the photons produced must have precise values.

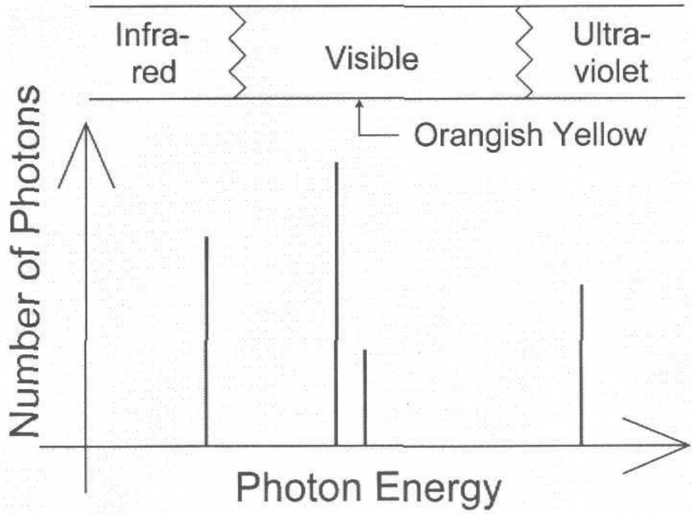


- For most energies, no photons are emitted. For those precise energies corresponding to allowed transitions, the number of photons emitted depends on details of atomic structure.

COLORED LIGHT FROM ATOMIC EMISSIONS

- If at least some of the photons generated have energies (wavelengths) falling in the visible range, light emissions will be detected by our eyes.

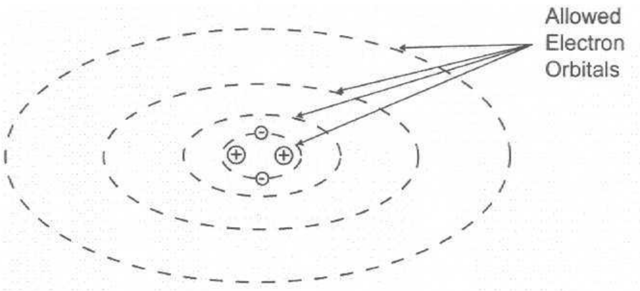
- If the photons with energies (wavelengths) falling in the visible range predominate in one portion of the visible spectrum, the light will appear colored.



- Because atoms of different elements have different allowed energy levels, they produce different energy photons — potentially different colored light.

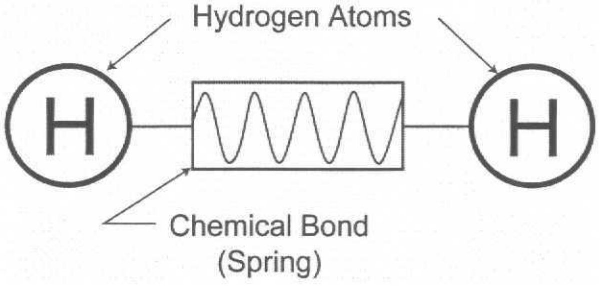
MOLECULAR QUANTUM THEORY (HYDROGEN MOLECULE)

- Molecules, with their orbiting electrons, are bound systems. Thus, molecules are quantized and may only exist in certain allowed electron energy states.



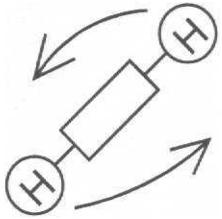
Hydrogen Molecule (H_2)
(in Ground State)

- However, in addition to electrons being bound to the molecule, the two hydrogen atoms are also bound to each other by a chemical bond.



POSSIBLE QUANTIZED MOLECULAR MOTIONS

- Rotational motion:



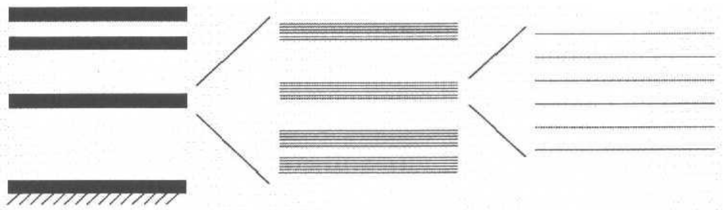
- Vibrational motions:
  - Bending:

  - Stretching:

- Because atoms are bound together in a molecule, atomic motions are also quantized. Thus, in addition to allowed electron energy levels, there are series of allowed energy levels for these motions.

MOLECULAR ENERGY LEVELS

- The spacing of electron energy levels is greatest. Vibrational energies are much smaller, thus these levels are much closer together. Rotational energies are still smaller and the levels even closer together.
- Molecules can exist in any of the allowed electron, vibrational and rotational levels. Thus the overall molecular energy level diagram appears much like that for an atom; however, on top of each electron level is a series of vibrational levels and on each of these is a series of rotational levels. The overall appearance is that of a series of bands of very closely spaced energy levels.



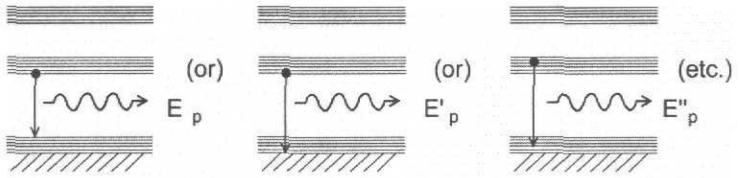
Molecular Energy Level Diagram (bands at each electron energy level)

Closer Look (bands at each vibrational energy level)

Still Closer Look (rotational energy levels)

ENERGY BAND TRANSITIONS

- With atoms, only one photon energy is possible for each electron transition. However, with molecules, bands of allowed energies are possible.
- This is because in molecules, transitions can occur between any of the large number of energy levels in one band and any of an equally large number of levels in another band.

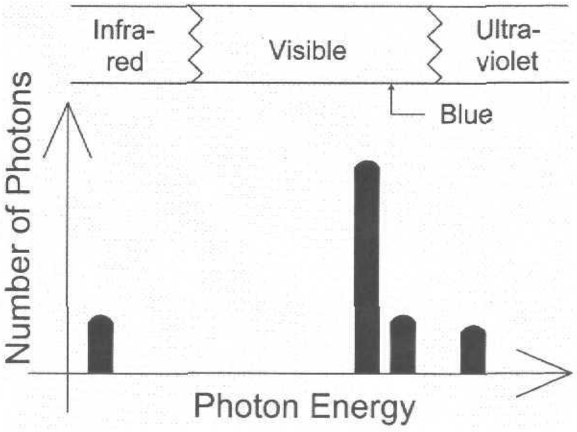


$$E_p \lesssim E'_p \lesssim E''_p$$

- Accordingly, an electron transition in a molecule is not restricted to producing just one single photon energy. Rather, a range of slightly different photon energies is possible for each electron transition.

MOLECULAR BAND SPECTRA

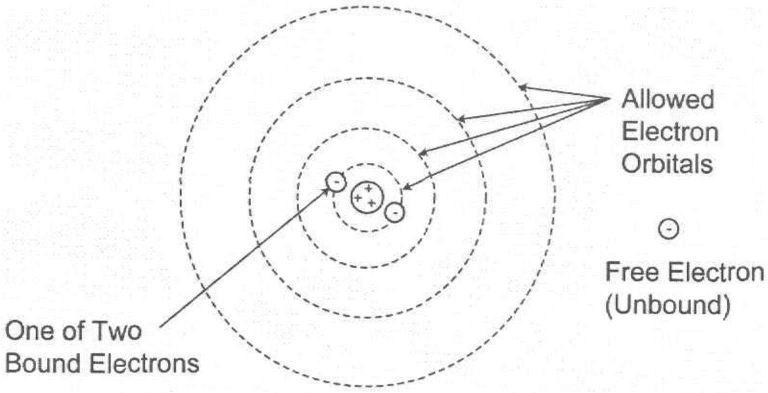
- A graph of photon energies from a molecule appears similar to that of an atom; except that bands — rather than lines — appear.
- If some of those bands fall in the visible range, then light emissions will be seen.
- If the bands in the visible range predominate in one region, then the light will appear colored.



- The number of photons emitted per band depends on the details of molecular structure.

ATOMIC IONS

- An ion is a charged atom and is produced when the atom loses one of its bound electrons. Those electrons remaining are still bound to the atom (quantized), but the lost electron ("free electron") is unbound and free to leave the vicinity of the atom.

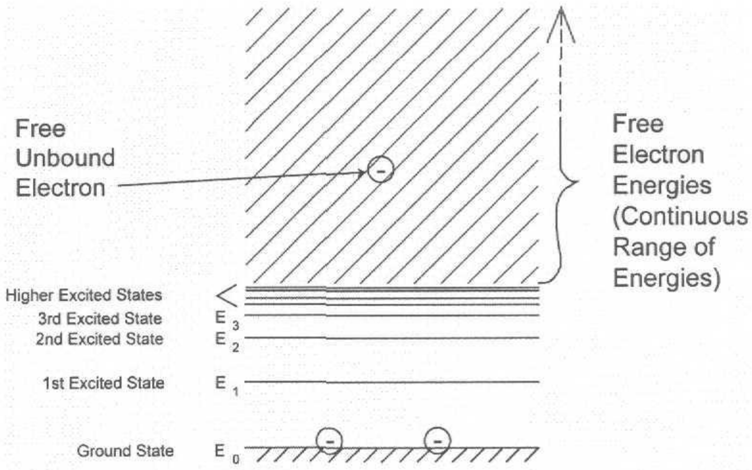


Lithium 1+ Ion
(in ground state)

- Unbound electrons are not quantized. Thus they can have any amount of energy.

ENERGY LEVEL DIAGRAM FOR IONS

- Above the highest energy level for bound electrons is a continuous range of allowed energies for free electrons.



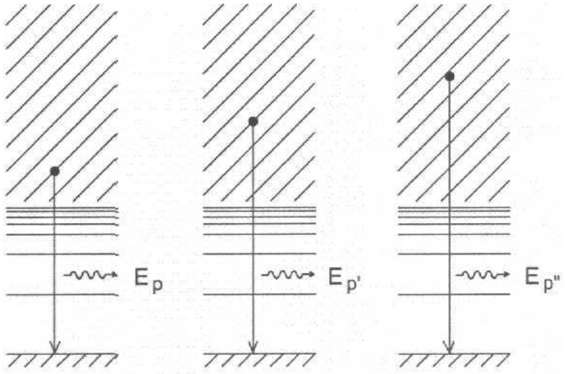
Lithium 1+ Ion Plus Free Electron Energy Level Diagram

- An electron possessing any of these free electron energies is no longer bound to the atom. In this manner, an ion (charged atom) and a free electron are formed.

IONIC SPECTRA

- For the remaining bound electrons, line spectra are produced in just the same way as for atoms. However, the energy levels will be slightly different and the light produced by electron transitions will be different in color than that from the neutral (non-ionized) atoms.

- Ion recombination is when a free electron returns and binds to the ion. Because the free electron can start with any amount of energy, this produces a continuous range of photon energies.

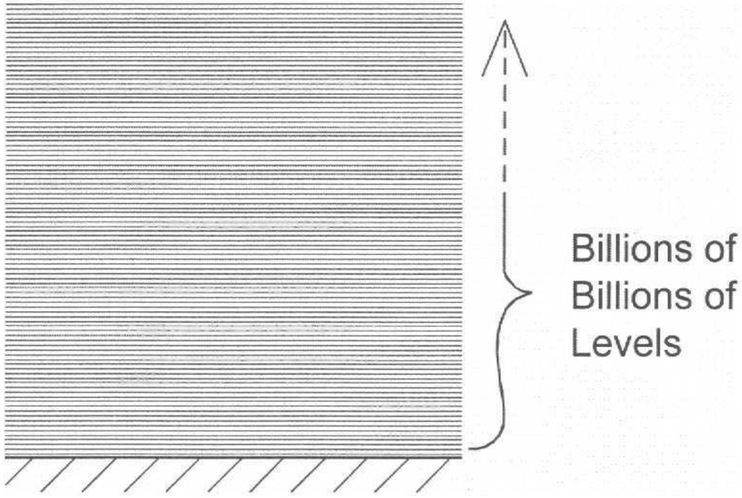


$E_p < E_{p'} < E_{p''}$

PARTICLE ENERGY LEVELS

- Tiny liquid and/or solid particles are produced and exist in nearly all flames. Even the smallest visible particle is an agglomeration of an enormous number of atoms.

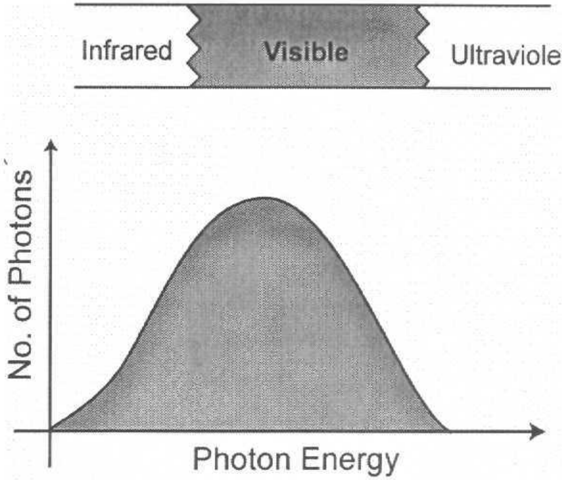
- The result of having so very many atoms in a smoke particle is to have an energy level diagram with incredibly many levels.



- Because of the myriad of energy levels, an incandescent particle produces a continuous range of photons from near zero to very high energies.

CONTINUOUS SPECTRA

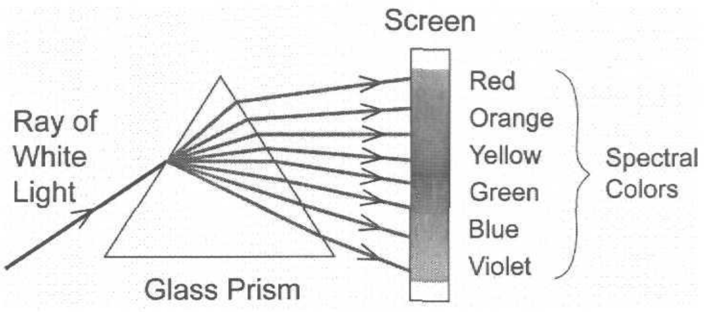
- Because of the wide range of very narrowly spaced or continuous energy levels associated with incandescent particles or ion recombinations, only a continuous spectrum of photon energies can be produced.



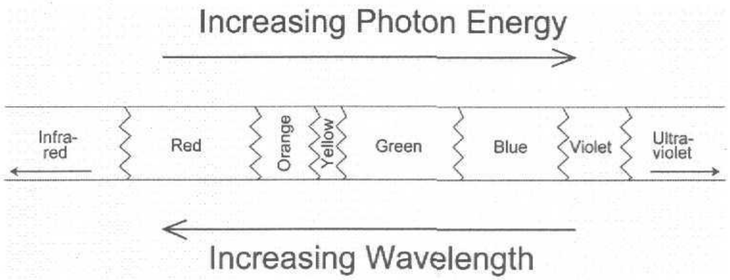
- Because of the very nature of continuous spectra at the temperature of colored flames, it is not possible for photon energies to predominate in any one portion of the visible spectrum. Thus sources of continuous light emissions can not generate colored light and are always undesirable when attempting to produce deeply colored flames.

NEWTON'S OBSERVATION OF THE VISIBLE LIGHT SPECTRUM

- Newton discovered that white light passing through a prism can produce a spectrum of colored light.

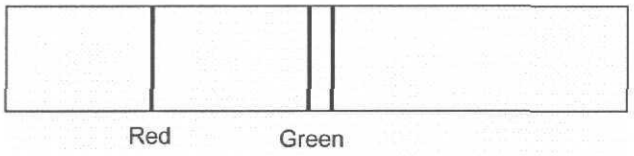


- Spectral light can be characterized by its wavelength (measured in nanometers = 10^{-9} meters).

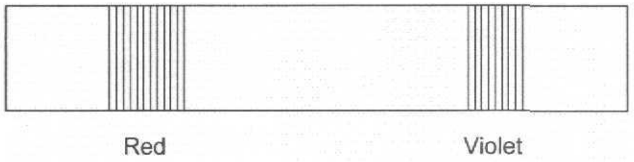


SPECTRA VIEWED USING NEWTON'S APPARATUS

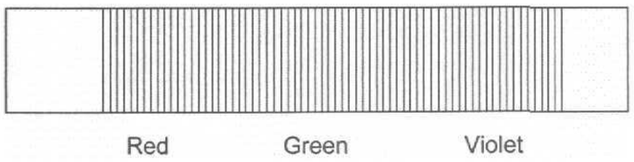
- When light emissions from atoms, molecules and incandescent particles are passed through a narrow slit and viewed using a prism, they will have substantially different appearances.
  - Atomic line spectra



  - Molecular band spectra



  - Continuous spectra



CHROMATICITY DIAGRAM

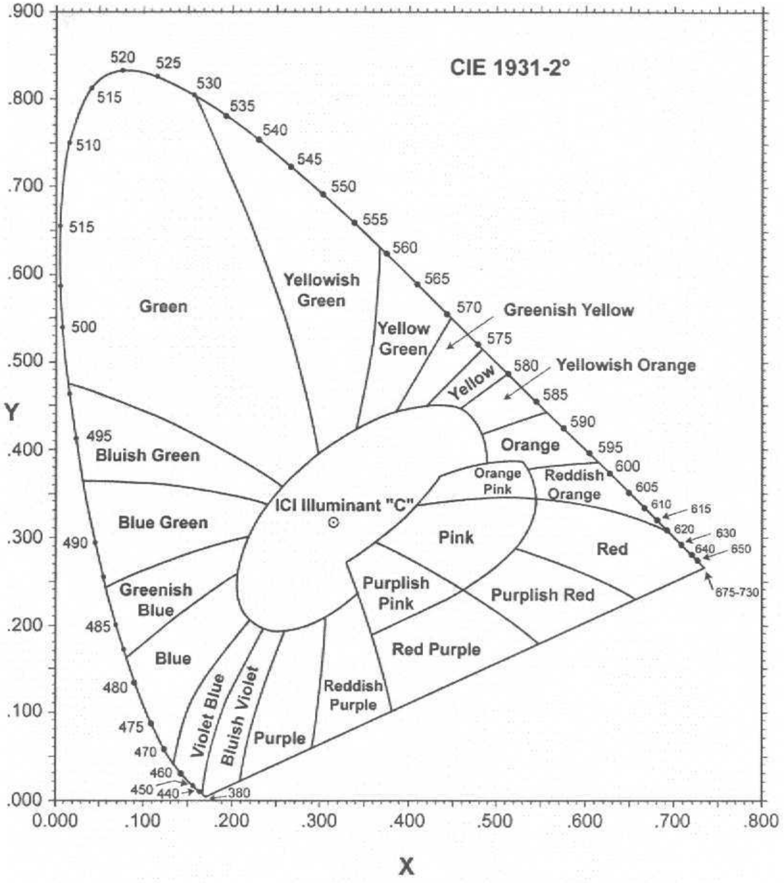
- Newton also discovered that the blending of pure spectral colors produced new "composite" colors. He found that blending only spectral red, green and blue light in various proportions produced essentially all other colors. Thus, these three colors are commonly called the "primary" colors.

- Newton also observed that it was only the relative intensities (ratios) of the three primary colors that determined what color would be produced. Collectively varying the intensity of the primary colors only changed the intensity of the "composite" color. It did not change its color.

- Color only exists in the brain of the viewer, it is a psychological response to a physical stimulus (i.e., it cannot be measured with an instrument).

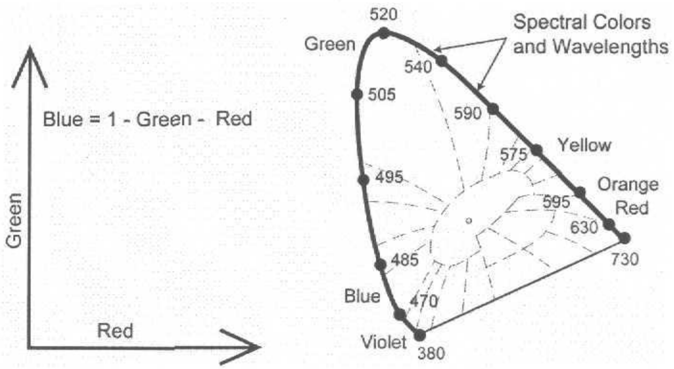
- An efficient method was needed to deal with additive color mixing. That turned out to be what is now commonly called a "chromaticity" diagram, which is a special graph upon which all possible spectral and composite colors can be located.

SAMPLE CHROMATICITY DIAGRAM



CHROMATICITY DIAGRAM (Continued)

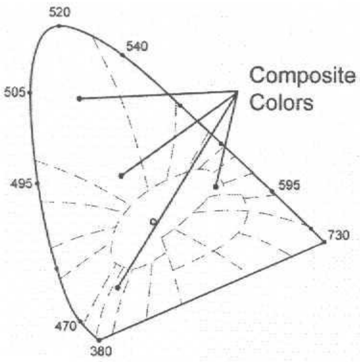
- This standard chromaticity diagram was established by the International Commission on Illumination (ICI) in 1931.
- The two axes listed are the fraction of special primary red and special primary green light used to make a given color.
  - Because the fractions must add to one, the amount of blue light is implicit.

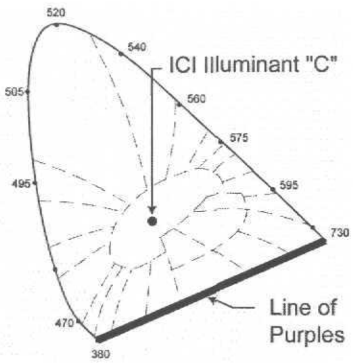


- Newton's spectral colors lie along the tongue-shaped perimeter of the diagram. The numbers listed are the wavelengths corresponding to the spectral colors.

CHROMATICITY DIAGRAM (Continued)

- All of the composite colors that can be made by combining various spectral colors, lie inside the tongue-shaped perimeter. The more pure composite colors lie near the perimeter and white lies in the middle.

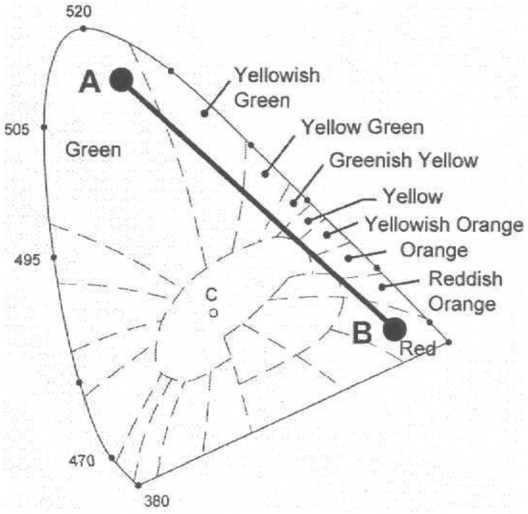




- The dot at ICI Illuminant "C" approximates typical daylight at noon.
- The "line of purples" lies across the bottom of the diagram. These are the only pure, non-spectral colors.

CLASSICAL LAWS OF COLOR MIXING

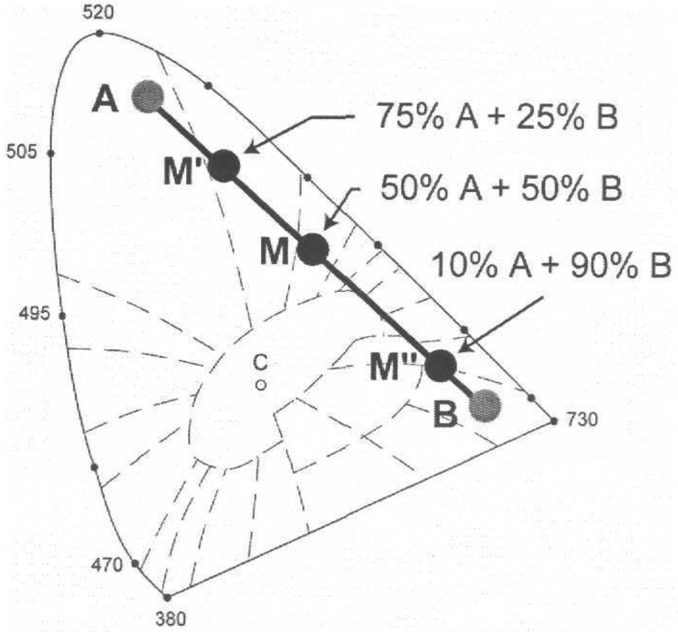
- **First Law: Every color is represented by a definite "color point" in the color region of the chromaticity diagram. For example, medium purity green and red light have color points A and B, respectively.**



- **Second Law: When two color light sources are combined in various proportions, the resulting color points lie along the "color line" connecting the two original color points. For example, when colors A and B are added together, only those colors along the line AB can be produced.**

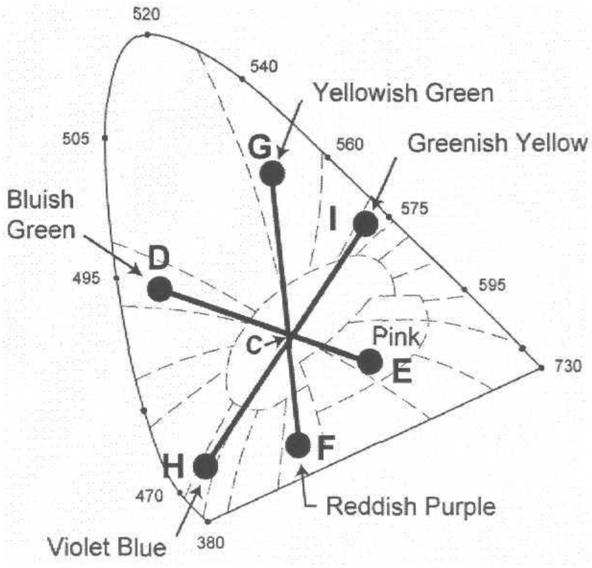
CLASSICAL LAWS OF COLOR MIXING (Continued)

- **Second Law (Continued): The color point (M) made by mixing two colors (A & B) lies a distance along the color line that is proportional to the intensity of each source.**



CLASSICAL LAWS OF COLOR MIXING (Continued)

- **Third Law: Every color except pure spectral colors can be made from any of a large number of combinations of color sources, and those composite colors produced will appear indistinguishable to an observer.**

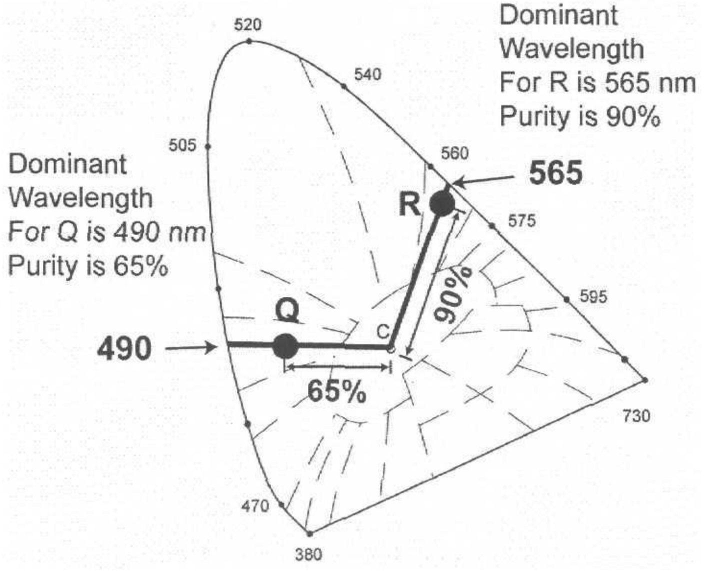


- **Illuminant C (white light) can be made from sources of bluish green and pink light (D and E), reddish purple and yellowish green (F and G), purplish blue and greenish yellow (H and I), or any pair of colors whose color line passes through color point "C".**

DOMINANT WAVELENGTH AND PURITY

- **Colors can be defined (quantified) by specifying their "dominant wavelength" and "purity".**

- **Dominant wavelength can be found by drawing a line from ICI "C" through the color point to the boundary of the chromaticity diagram. The dominant wavelength is the spectral wavelength read at that point.**



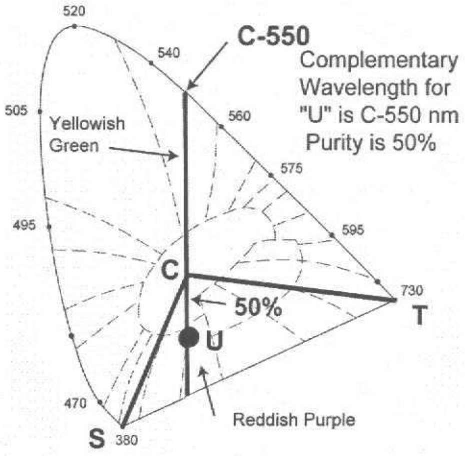
Dominant Wavelength For R is 565 nm Purity is 90%

Dominant Wavelength For Q is 490 nm Purity is 65%

- **Purity is the relative percentage of the distance from ICI "C" to the color point.**

NON-SPECTRAL COLORS

- **Non-spectral colors are those falling inside the triangle STC. They are defined by their "complementary wavelength" and purity.**



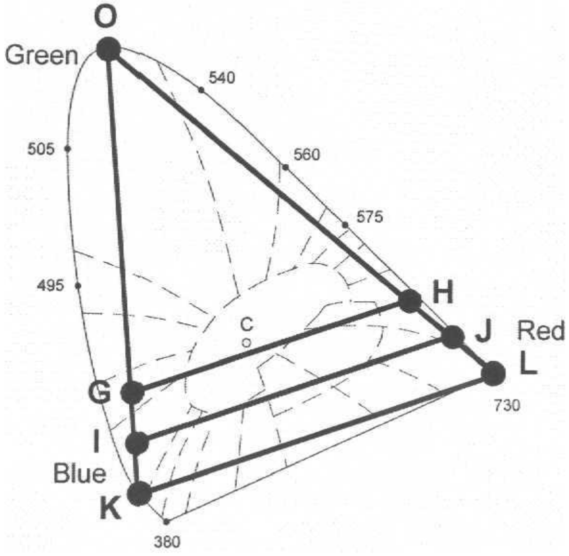
Complementary Wavelength for "U" is C-550 nm
Purity is 50%

- **The complementary wavelength can be found by drawing a line from the color point, through ICI "C" to the boundary of the chromaticity diagram. The complementary wavelength is the spectral wavelength read at that point.**

- **To determine purity, the line is extended to the bottom of the chromaticity diagram. Purity is the relative percentage of the distance from ICI "C" to the color point.**

COMPOSITE COLORS PRODUCED USING THE PRIMARIES

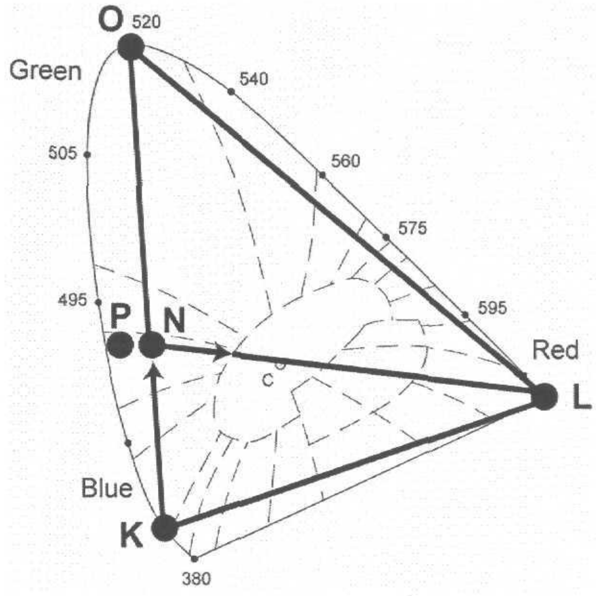
- **Most composite colors can be made using the three primary spectral colors: red, blue and green. All colors whose points fall inside the color triangle KLO can be made from various combinations of the spectral colors K, L, and O.**



- **For example, using various amounts of red and blue, any of those colors along the line KL can be made. If some green is added to the mix, colors along the line IJ can be made. If more green is added, colors along GH can be produced. In this way, all colors inside the triangle KLO can be made.**

COMPOSITE COLORS PRODUCED USING THE PRIMARIES (Continued)

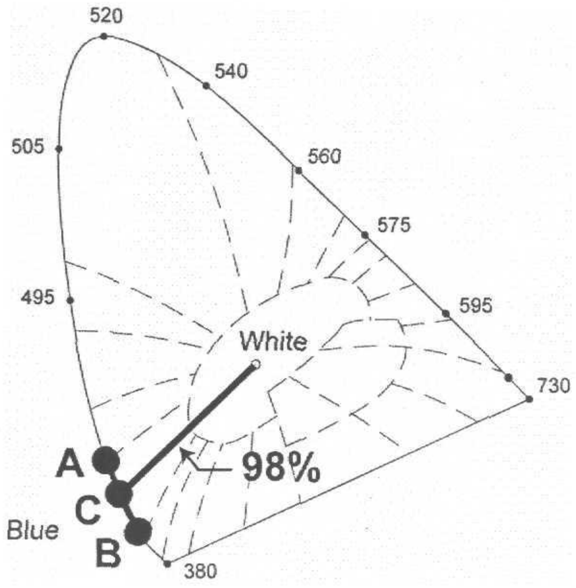
- **Some composite colors can not be made using the primary colors, specifically any color whose color point falls outside the color triangle KLO.**



- **For example, P cannot be made from combinations of K, L, and O. Using a mix of blue and green alone, color point N can be reached. When red is added, the color point moves along the line NL towards L. Thus to reach color point P, the amount of red needed is less than zero, and this is impossible.**

HIGH PURITY COLOR EMISSION FROM ATOMS

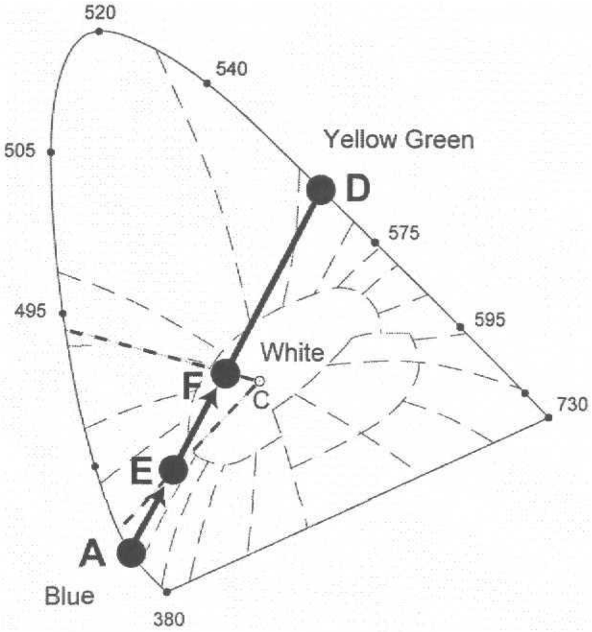
- **If an atom produced only one spectral line falling in the visible range, the color point would fall somewhere on the spectral color boundary of the chromaticity diagram and would have 100% (perfect) purity (e.g., color point A).**



- **If an atom had two spectral lines of about the same wavelength, there would be a small shift in the color of the emissions, but it would still result in near 100% purity (e.g., color point A and B combining to produce C).**

LOW PURITY COLOR EMISSION FROM ATOMS

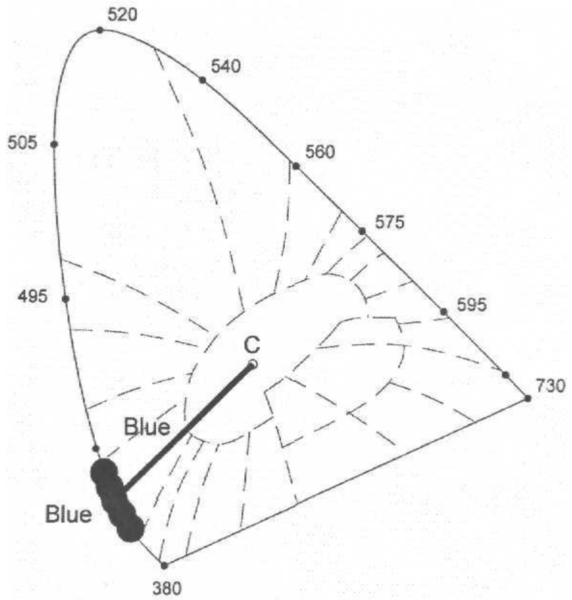
- **If an atom has two spectral lines of significantly different wavelengths, there can be a major shift in color that can result in a great loss of purity.**



- **For example, color points A and D can combine in various proportions to produce colors along the line AD. If the ratio of intensity of A and D are about 4:1, color point E will be produced. If the ratio is about 1:1, color point F, white, will be produced.**

COLOR EMISSIONS FROM MOLECULES

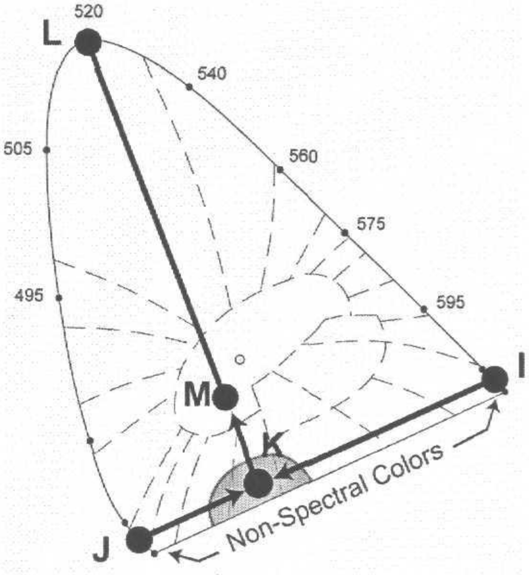
- **Molecular bands are roughly equivalent to multiple closely spaced atomic lines, and the result for a single band is a high purity composite color.**



- **If more than one band is produced, and the bands are widely separated, just like the low purity atomic example, the result can be a serious loss of color purity.**

NON-SPECTRAL COLOR PRODUCTION

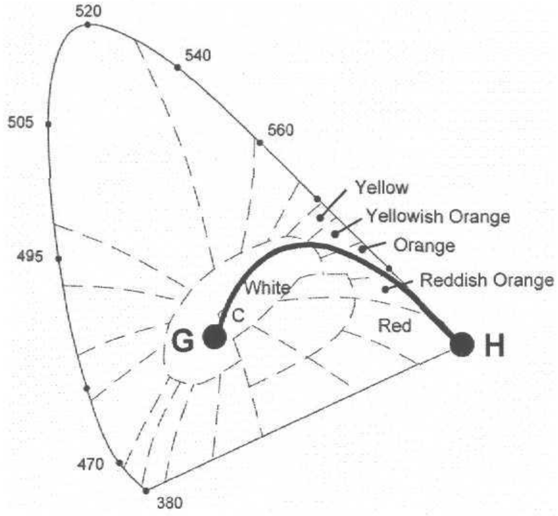
- **High purity, non-spectral colors can only be produced by properly balanced high purity red and violet light. For example, a ratio of purplish blue (J) to red (I) of about 2:1 produces the high purity purple color point (K).**



- **Even a small addition of green light (L) seriously reduces its purity. For example, if only about 20% of green (L) is added, the result is white light (M).**

INCANDESCENT EMISSIONS

- **When solids or liquids are heated to high temperatures, they glow (incandesce). The intensity and color of the light is a function of temperature.**

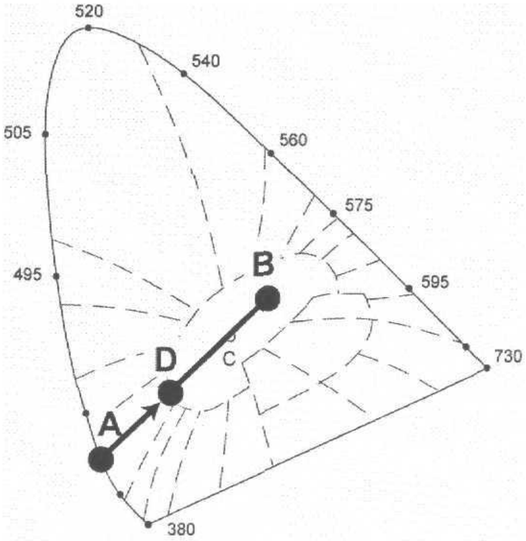


- **The color of ideal glowing bodies:**

	Temperature	Descriptive Color
	500 °C	Red
	850 °C	Reddish orange
	1500 °C	Orange
Flame ↑	2200 °C	Yellow-orangish white
Temps. ↓	3000 °C	White

LOSS OF PURITY FROM INCANDESCENCE

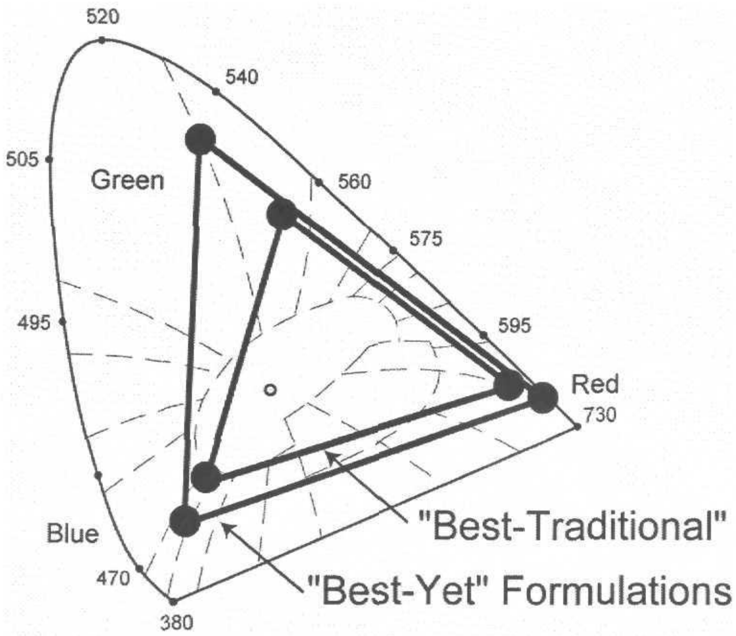
- Pyrotechnic flames always contain some solid or liquid particles, either ejected from the burning surface or as combustion products (smoke). At the temperatures of colored flame, these particles incandesce with near white light, reducing the purity of any colored light produced.



- For example, adding only a small fraction of incandescent light (B) to 100% purity blue light (A) will result in a significant reduction in its purity (D).

PRACTICAL LIMITS FOR COLORED FLAMES

- Pyrotechnic flames contain many atomic and molecular species, each capable of a number of different spectral emissions. In addition, there generally are sources of continuous emissions.



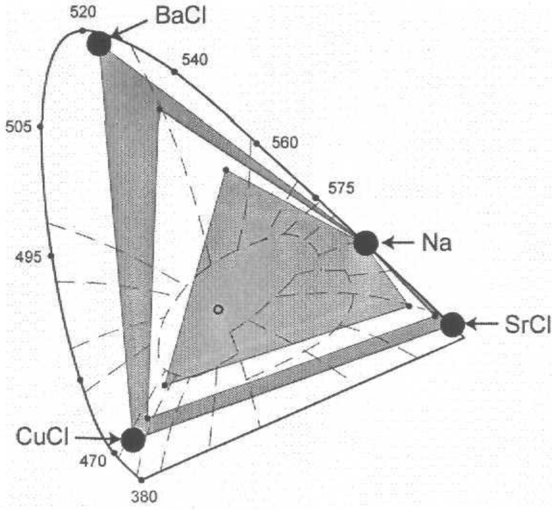
- When the color points from all the many sources are combined, truly high purity flame colors are generally not possible.

PYRO-COLOR HARMONY

[Baechle & Veline]

- **If truly excellent color formulations are derived for red, green and blue colors (The Veline system also uses orange.), <u>and</u> —**

- **If those formulations are completely compatible (i.e., can be mixed in any proportion without altering one another's ability to produce color), <u>then</u> —**



- **A very large variety of interesting colors can be made using ratios of just those formulations.**

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SECTION 7

CHEMISTRY OF COLORED FLAME

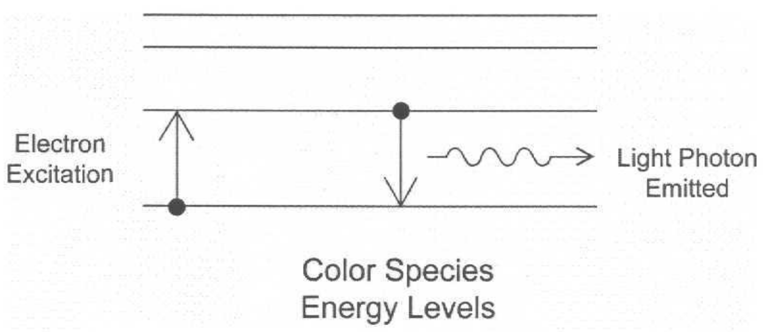
- Mechanism of Colored Light Production
- Color Agents and Color Species
- Basic Red Color Chemistry
- Optimizing Color Quality
- Green, Orange, Blue, Yellow and Purple
- Other Topics

GENERAL MECHANISM FOR PRODUCTION OF COLORED LIGHT

- The following general reaction occurs for colored light production in flames:

$$(CS) + \text{Energy} \leftrightarrow (CS)^* \rightarrow (CS) + \text{Photon}$$

[Here (CS) is the color species responsible for production of the color of light desired, and the * indicates when it is in an excited electron state.]



- Thus, in order to produce colored light, besides needing the color species, a source of energy is necessary. In pyrotechnics, the energy is typically thermal energy (heat).

ENERGY SOURCE FOR COLORED LIGHT PRODUCTION

- The source of energy, necessary to cause excitation of electrons in atoms and molecules in colored flames, is thermal energy from pyrotechnic combustion.

  Fuel + oxidizer → products + heat

- Common fuels and oxidizers used in color stars:

Fuels	Symbol
Aluminum	Al
Carbon (Charcoal, ≈80% C)	C
Magnesium	Mg
Magnalium	Mg/Al
Red gum (Accroides)	Complex
Shellac	Complex
Oxidizers	**Symbol**
Ammonium perchlorate	NH_4ClO_4
Barium chlorate	$Ba(ClO_3)_2$
Barium nitrate	$Ba(NO_3)_2$
Potassium chlorate	$KClO_3$
Potassium nitrate	KNO_3
Potassium perchlorate	$KClO_4$
Sodium nitrate	$NaNO_3$
Strontium nitrate	$Sr(NO_3)_2$

AMOUNT OF ENERGY PRODUCED BY COMBUSTION

- The choice of oxidizer and fuel determines the amount of heat produced during combustion. One unit for heat is the kilocalorie (kcal) and is often expressed as kcal/g (per gram) of material.

- The amount of energy released by some common oxidizers using carbon for fuel and forming CO_2 as its product are listed below:

Oxidizer	Symbol	Heat of Reaction ($kcal/g_{ox}$)
Potassium perchlorate	$KClO_4$	1.4
Ammonium perchlorate	NH_4ClO_4	1.3
Potassium chlorate	$KClO_3$	1.2
Strontium nitrate	$Sr(NO_3)_2$	0.7
Barium nitrate	$Ba(NO_3)_2$	0.5
Potassium nitrate	KNO_3	0.4

- Note that these oxidizers can be divided into relatively high energy producers and relatively low energy producers.

AMOUNT OF ENERGY PRODUCED BY COMBUSTION (Continued)

- **The amount of energy released by combustion of some fuels** [Conkling]

Fuel	Symbol	Heat of Combustion (kJ/g_{fuel})
Carbon	C (graphite)	1.9
Aluminum	Al	1.8
Magnalium	Mg/Al	1.6
Magnesium	Mg	1.4
PVC	(CH_2CHCl)	1.1
Dextrin	$(C_6H_{10}O_5)_n \cdot H_2O$	1.0
Lactose	$C_{12}H_{22}O_{11} \cdot H_2O$	0.9
Sulfur	S	0.5

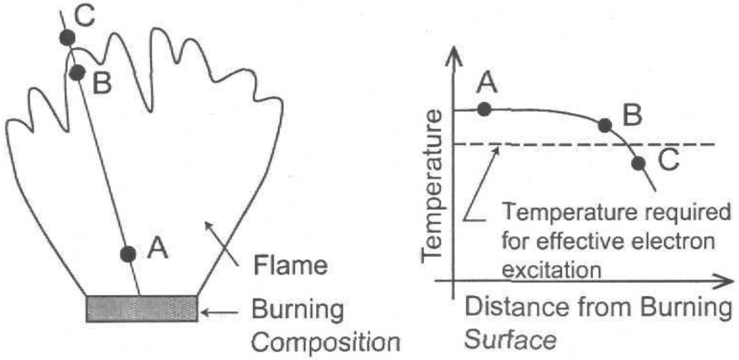
- **Note that these fuels can be divided into relatively high energy producers and relatively low energy producers.**

- **Note that while carbon (as graphite) is a high energy fuel, it often seems not to be. This may be because carbon does not melt (like metals) before combusting.**

PYROTECHNIC FLAME — MANIFESTATION OF THERMAL ENERGY

- **Thermal energy from pyrotechnic combustion can be manifested in the form of a flame, which is a high *temperature region seen as a result of its emission* of visible light.**

- **The flame envelope is roughly the boundary that is seen as the "flame".**



- **For the most part, the chemical species and temperature just inside (B) and just outside (C) the flame envelope are not vastly different. However, the differences are great enough to significantly affect the extent to which visible light is emitted.**

FLAME TEMPERATURES

- **It has generally been believed that colored light cannot be produced effectively unless the flame temperature exceeds about 2000 °C.**

- **Examples of flame temperature for various oxidizers and shellac (as fuel) with 10% sodium oxalate (which is necessary to optically measure flame temperature)** [Shimizu].

Oxidizer	%	Fuel	%	Flame Temperature
Potassium perchlorate	74	Shellac	16	2247 °C
Ammonium perchlorate	76	Shellac	14	2207 °C
Potassium chlorate	77	Shellac	13	2177 °C
Potassium nitrate	72	Shellac	18	1697 °C

- **For the oxidizers listed, it would be expected that only potassium nitrate would not produce the flame temperature necessary for useful color production. (However, recent work by Jennings-White has shown that colors are possible using non-metal fuels with nitrate oxidizers.)**

ELEMENTS COMMONLY USED TO GENERATE COLORED PYROTECHNIC FLAMES

- **The elements commonly associated with colored flame are the metals listed below** [Douda].

Element	Color	Color Generating Species	Approximate (equivalent) Wavelength (nm)
Strontium	Red	SrCl	630
	Red orange	SrOH	610
Barium	Green	BaCl	520
	Green	BaOH	weak
Copper	Violet blue	CuCl	450
	Yellowish-green	CuOH	540
Calcium	Orange	CaOH	600
	Red orange	CaCl	610
Sodium	Yellow	Na^{o} (atoms)	589

- **Note that, except for sodium, the elements themselves that are not the color generating species, but rather molecular combinations with Cl and OH.**

COMMONLY USED COLOR AGENTS

- Below is a list of commonly used color agents:

Color	Color Agent	Formula
Red	Strontium carbonate	$SrCO_3$
	Strontium nitrate	$Sr(NO_3)_2$
	Strontium oxalate	SrC_2O_4
	Strontium sulfate	$SrSO_4$
Green	Barium carbonate	$BaCO_3$
	Barium nitrate	$Ba(NO_3)_2$
	Barium sulfate	$BaSO_4$
Blue	Copper(I) chloride	$CuCl$
	Copper(II) carbonate	$CuCO_3$
	Copper(II) oxide	CuO
	Copper(II) oxychloride	$CuCl_2 \cdot 3Cu(OH)_2$
Orange	Calcium carbonate	$CaCO_3$
	Calcium oxalate	CaC_2O_4
	Calcium sulfate	$CaSO_4$
Yellow	Cryolite	Na_3AlF_6
	Sodium nitrate	$NaNO_3$
	Sodium oxalate	$Na_2C_2O_4$

- Note that these color agents are not the color generating species listed previously.

PRODUCTION OF COLOR GENERATING SPECIES

- Most color species are not stable chemicals under normal conditions. They cannot be used directly as color agents and must be formed in the flame.

- The likely production mechanism is:
  - Initial step:

$$SrCO_{3(s)} + \text{heat} \leftrightarrow SrO_{(s)} + CO_2$$

  - Production of color species:

$$SrO + HX \leftrightarrow SrOH^{\bullet} + X^{\bullet}$$

(HX is water, a hydrocarbon, alcohol, etc.)
(The "•" indicates a free radical species.)

$$SrOH^{\bullet} + Cl^{\bullet} \leftrightarrow SrCl^{\bullet} + OH^{\bullet}$$

- Note that hydrogen chloride is produced upon the burning of ammonium perchlorate and also from the burning of some chlorine donors.
  - Thus as an alternative:

$$SrO + HCl \leftrightarrow SrCl^{\bullet} + OH^{\bullet}$$

SOURCES OF $CL^\bullet$ AND HCL FOR COLOR SPECIES

- Potassium chlorate or potassium perchlorate can produce $Cl^\bullet$, but that reaction is not energetically preferred.

$$KClO_4 + 2\,C \rightarrow KCl + 2\,CO_2 + 1.4\ \text{kcal/g}_{ox}$$

$$4\,KClO_4 + 2\,C \rightarrow 2\,K_2O + 7\,CO_2 + \underline{4\,Cl^\bullet} + 0.5\ \text{kcal/g}_{ox}$$

- Chlorine donors such as PVC:

$$8\,(-CH_2CHCl-) + 11\,KClO_4 \rightarrow 11\,KCl + 16\,CO_2 + 12\,H_2O + \underline{8\,Cl^\bullet}$$

- Ammonium perchlorate serves as a source of HCl, but burn rates are generally low.

$$4\,NH_4ClO_4 + C \rightarrow 2\,N_2 + 6\,H_2O + 5\,CO_2 + \underline{4\,HCl}$$

- The too dangerous combination of potassium chlorate and sulfur:

$$2\,KClO_3 + 2\,S \rightarrow K_2SO_4 + SO_2 + Cl_2$$

CHLORINE DONORS

- Chlorine donors (also called color enhancers) are chlorine rich materials added to colored flame compositions to aid in the production of the desired color emitting species.

Chlorine Donor	Formula	Percent Chlorine
Dechlorane +	$C_{10}Cl_{12}$	78
HCB (hexachlorobenzene) *	C_6Cl_6	74
Saran resin	$(C_3H_2Cl_2)_n$	73
BHC (benzene hexachloride) *	$C_6H_6Cl_6$	73
Parlon	$(C_5H_6Cl_4)_n$	68
Chlorowax	variable	40–70
PVC (polyvinyl chloride)	$(C_2H_3Cl)_n$	57
Calomel (mercury(I) chloride)	Hg_2Cl_2	15

\+ Relatively poor fuel.

* Avoid HCB and BHC because of suspected carcinogenicity. (Benzene hexachloride is more correctly termed hexachlorocyclohexane.)

SOURCE OF OH$^\bullet$ FOR PRODUCING COLOR SPECIES

- Whenever a hydrogen containing fuel is burned, *water vapor is produced.*

$$3\ KClO_4 + \underset{\text{(Dextrin)}}{(C_6H_{10}O_5)_n} \rightarrow 3\ KCl + 5\ H_2O + 6\ CO_2 + \text{heat}$$

- At the high temperature of a flame, water reacts to produce the color species.

$$SrO + H_2O \rightarrow SrOH^\bullet + OH^\bullet$$

- Because dextrin or some other hydrogen containing binder is almost always used in stars, some production of the monohydroxide generally results.
- However, recall that generally the monochloride is preferred over the monohydroxide as the color emitting species.

BASIC CHEMISTRY FOR RED FLAME

- The source of thermal energy is combustion.

$$KClO_4 + 2\ C \rightarrow KCl + 2\ CO_2 + \text{heat}$$

- Decomposition and vaporization of color agent.

$$SrCO_3 + \text{heat} \rightarrow SrO_{(g)} + CO_2$$

- *Production of color species.*

$$SrO_{(g)} + HCl \rightarrow SrCl_{(g)} + OH$$

$$SrO_{(g)} + H_2O \rightarrow SrOH_{(g)} + OH$$

- Electron excitation (denoted by the *).

$$SrCl_{(g)} + \text{heat} \rightarrow SrCl_{(g)}{}^*$$

$$SrOH_{(g)} + \text{heat} \rightarrow SrOH_{(g)}{}^*$$

- De-excitation, with light production.

$$SrCl_{(g)}{}^* \rightarrow SrCl_{(g)} + \text{photon (~630 nm, red)}$$

$$SrOH_{(g)}{}^* \rightarrow SrOH_{(g)} + \text{photon (~610 nm, red/orange)}$$

COMPETING CHEMICAL REACTIONS

- **Simplified strontium chemistry for red flame can be linked as shown** [Douda]:

$$\begin{tikzcd}
\mathrm{SrCO_3} \arrow[d] & & & & \\
\mathrm{SrO_{(s)}} \arrow[r, leftrightarrow] & \mathrm{SrO_{(l)}} \arrow[r, leftrightarrow] & \mathrm{SrO_{(g)}} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow, "\mathrm{HCl}"] & \mathrm{Sr^0_{(g)}} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow, "\mathrm{Cl^\bullet}"] & \mathrm{Sr^+} \\
\mathrm{SrCl_{2(s)}} \arrow[r, leftrightarrow] & \mathrm{SrCl_{2(l)}} \arrow[r, leftrightarrow] & \mathrm{SrCl_{(g)}} \arrow[r, leftrightarrow] & \mathrm{SrCl^*} \arrow[d] & \\
& & & \text{(Red light photon)} &
\end{tikzcd}$$

- **Note: at the temperatures of colored flames, when strontium atoms are ionized, it will only be to the +1 state and not the +2 state.**

- **It is important to note that steps from left to right (and generally steps from top to bottom) consume energy.**

- **For high quality red light production, it is only $SrCl_{(g)}$ that is useful. All the other species present act to weaken the purity of the color.**

UNDESIRABLE CHEMICAL SPECIES IN RED FLAME

- **Undesirable chemical species generally weaken the purity of flame color by producing other than red colored light.**

Chemical Species	Detrimental Effect
$SrCl_{2(l)}$ or $SrCl_{(s)}$	Incandescent emissions, continuous spectrum
Sr^0 (atom)	Blue-violet color
Sr^{2+} (ion)	Violet color plus continuous spectrum from ion recombination
$SrO_{(g)}$	Orange color
$SrO_{(l)}$ or $SrO_{(s)}$	Incandescent emissions, continuous spectrum

- **For high purity color it is necessary to control flame chemistry. One must maximize the production of favorable species and minimize the production of undesirable species.**

BASIS FOR CONTROLLING COLORED FLAME CHEMISTRY

- *Within small regions in a flame at any given time,* there is an approximate state of chemical equilibrium between the chemical species present in that region.

$$SrO + HCl \leftrightarrow SrCl + OH^{\bullet}$$

- The state of equilibrium is indicated by the double headed arrow [↔]. This can be taken to mean that the rate of the reaction to the right, to form strontium monochloride, is equal to the reaction rate to the left.

- Chemical equilibrium provides the mechanism potentially to control flame chemistry. This is expressed by LeChâtelier's Principle:

> *Chemical systems in equilibrium respond to a stress in a manner that tends to relieve the stress.*

LECHÂTELIER'S PRINCIPLE APPLIED TO BASIC RED FLAME CHEMISTRY

- *Favorable red flame reactions:*

(1) $SrCO_3 + \text{heat} \leftrightarrow SrO_{(s)} + CO_2$

(2) $SrO_{(s)} + \text{heat} \leftrightarrow SrO_{(l)}$

(3) $SrO_{(l)} + \text{heat} \leftrightarrow SrO_{(g)}$

(4) $SrO_{(g)} + HCl \leftrightarrow SrCl_{(g)} + OH$

(5) $SrCl_{(g)} + \text{heat} \leftrightarrow SrCl_{(g)}^{*}$ (* denotes excited state)

(6) $SrCl_{(g)}^{*} \rightarrow SrCl_{(g)} + \text{photon } (\sim 630 \text{ nm})$

Favorable Conditions	Eq.	Makes More
More $SrCO_3$	1	$SrO_{(s)}$
More heat (higher flame temp.)	1–3	$SrO_{(g)}$
More HCl (more chlorine donor)	4	$SrCl_{(g)}$
More heat	5	$SrCl_{(g)}^{*}$

LECHÂTELIER'S PRINCIPLE APPLIED TO BASIC RED FLAME CHEMISTRY (Continued)

- Some unfavorable red flame reactions:

(1) $SrCl_{(g)}^* + heat \leftrightarrow Sr_{(g)} + Cl$

(2) $Sr_{(g)} + heat \leftrightarrow Sr^{2+} + 2e^-$

(3) $Sr_{(g)} + O \leftrightarrow SrO_{(g)}$

(4) $SrCl_{(g)} + Cl \leftrightarrow SrCl_{2(l)} + heat$

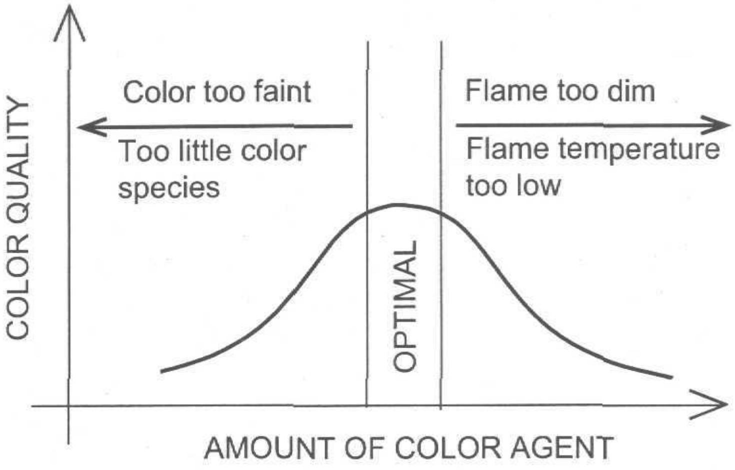
Favorable Conditions	Eq.	Effect
Less heat	1	Loses less $SrCl_{(g)}^*$
More Cl	1	Loses less $SrCl_{(g)}^*$
Less heat	2	Makes less Sr^{2+}
More e^-	2	Makes less Sr^{2+}
Less O	3	Makes less $SrO_{(g)}$
Less Cl	4	Makes less $SrCl_{2(l)}$
More heat	4	Makes less $SrCl_{2(l)}$

OPTIMIZING COLOR QUALITY

- To some extent by adjusting flame formulations, LeChâtelier's Principle can be used to favor production of desirable color species and reduce production of undesirable species.
- Control of flame chemistry can be accomplished by adjusting:
  - Amount of color agent.
  - Type of color agent.
  - Amount of chlorine donor.
  - Fuel/oxidizer ratio.
  - Flame temperature (type of fuel).
- However, there is no "free lunch". These adjustments can improve color quality, but they all have potentially adverse effects, too. The trick is to proceed only so far as benefits outweigh adverse effects.

AMOUNT OF COLOR AGENT

- As more color agent ($SrCO_3$) is used, it may be possible to make more SrCl. However, the heat consumed in the process of the decomposition of $SrCO_3$, will cause the flame to become dimmer.



- To maximize performance:
  - Can use metal fuels.

    Oxidizer + Metal Fuel → More Heat

    (Flame temperature is increased by as much as ≈800 °C. This additional heat can be used to vaporize more color agent.)

  - Can use color agent that does double duty.

"DOUBLE DUTY" COLOR AGENTS

- If a color agent is chosen that performs one of the other necessary functions in a colored flame, generally there is a reduction in the energy consumed.
  - Color agent (strontium nitrate) as oxidizer:

    $$Sr(NO_3)_2 + \text{fuel} \rightarrow SrO_{(g)} + \text{oxidized fuel} + \text{heat}$$

  - Color agent as fuel (strontium benzoate):

    (Sr Benz.)

    $$\text{Oxidizer} + SrC_7H_5O_2 \rightarrow SrO_{(g)} + \text{comb. prod.} + \text{heat}$$

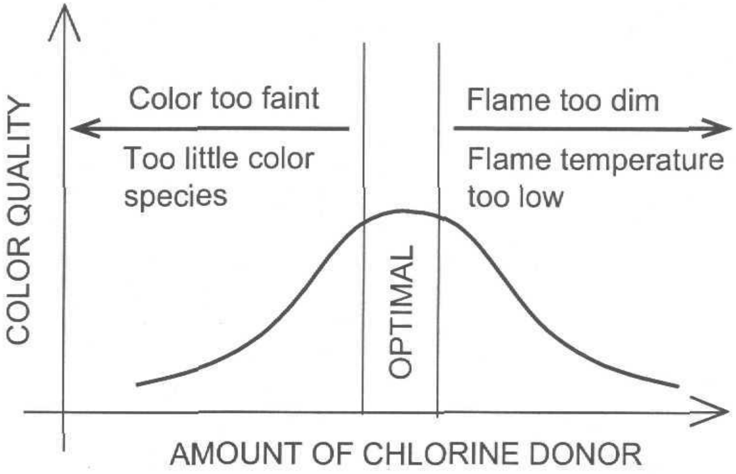
  - Color agent (strontium fluoride) as color enhancer:

    $$SrF_2 + \text{heat} \rightarrow SrF_{(g)} + F^{\bullet}$$

(Note that other members of chemical Group VII, such as fluorine, can act as color enhancers similar *to chlorine.)*

AMOUNT OF CHLORINE DONOR

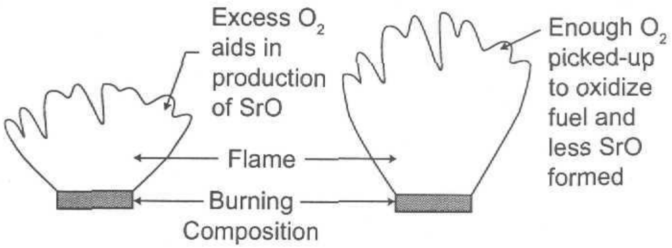
- As more chlorine donor is used, the production of SrCl is favored, but less heat is usually produced.



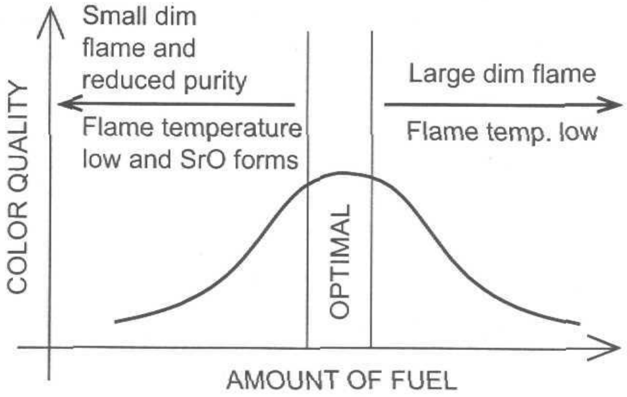
- To maximize performance:
  - Can use chlorine donor with higher percent Cl.
    PVC = 57% Saran resin = 73%
  - Can use metal fuel.
    oxidizer + metal fuel → more heat
  - Can use chlorine donor that is a higher energy fuel (not well reported in literature).

FUEL TO OXIDIZER RATIO

- As more fuel is used:
  - At first, flame envelope enlarges as atmospheric O_2 is consumed. Also, less SrO is produced in flame tips.

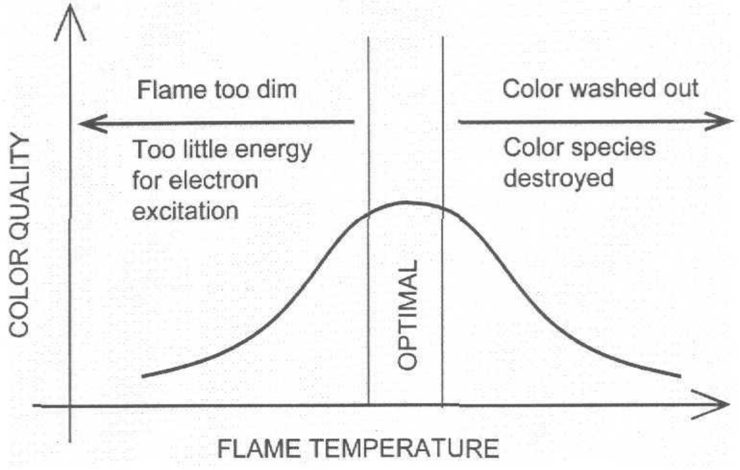


  - Then, flame temperature becomes seriously lower, because the energy produced is lowered as the oxidizer deficiency becomes excessive.



FLAME TEMPERATURE

- **As flame temperature is raised, the intensity of emitted light greatly increases, but high temperature may cause the destruction of the color species.**



- **To some extent, higher temperatures can be tolerated if high concentrations of Sr and Cl are present to stress the reaction to reduce the loss of $SrCl_{(g)}$. This can be accomplished by the use of more color agent and chlorine donor.**

RED STAR FORMULATIONS

- **These principles can be applied in newer red star formulations.**

Ingredient	Traditional	Modern	Advanced
Potassium chlorate	66	—	—
Potassium perchlorate	—	66	—
Strontium nitrate	—	—	60
Strontium carbonate	11	12	—
Charcoal (fine)	11	2	—
Red gum (or shellac)	8	13	3
Magnalium (fine)	—	—	12
PVC	—	2	—
Parlon	—	—	25
Dextrin (or rice starch)	4	5	—

- **Modern:**
  - **Safer oxidizer (potassium perchlorate).**
  - **Use of some chlorine donor (PVC).**
- **Advanced:**
  - **Oxidizer is color agent (strontium nitrate).**
  - **High energy metal fuel (magnalium).**
  - **Large amount of chlorine donor (Parlon™).**
  - **Fuel rich.**

GREEN AND ORANGE FLAMES

- Barium and calcium are in the same chemical group as strontium (Group II), thus their chemistries are all essentially the same.
  - For barium green flames, simply substitute Ba for Sr everywhere in the discussion of strontium red flames.
  - For calcium orange flames, CaCl is OK as a color species, but CaOH is the preferred color species. Other than that, all else is the same as for strontium red flames.

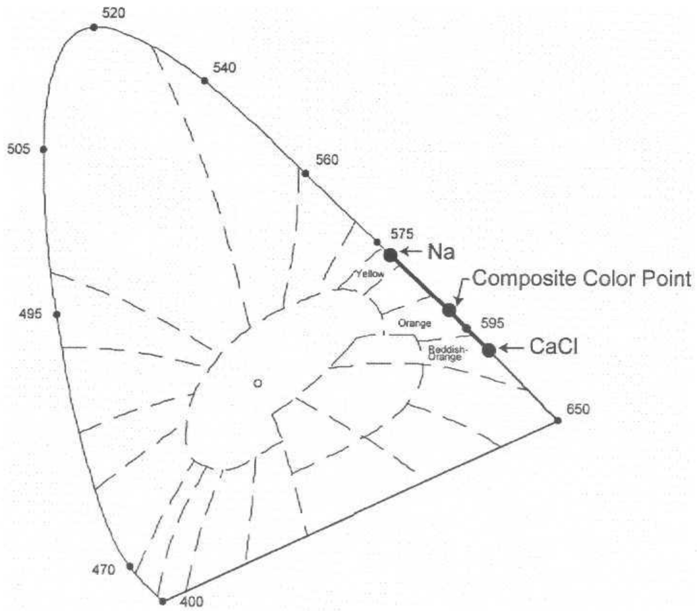
    CaCl → Reddish orange (~610 nm)

    CaOH → Borderline orange (~600 nm)
  - A hydrogen containing fuel such as red gum or dextrin, when used as one fuel, will serve as a color enhancer as it will produce H_2O when burned.

    $KClO_4$ + carbohydrate → $H_2O + CO_2$ + heat

IMPROVED ORANGE FLAME

- Jennings-White and Wilson did extensive work on orange flame. They found it to be effective to:
  - Encourage the production of CaCl to produce reddish orange flame.
  - Use cryolite (which releases Na – producing yellow) to shift the color to high purity orange.

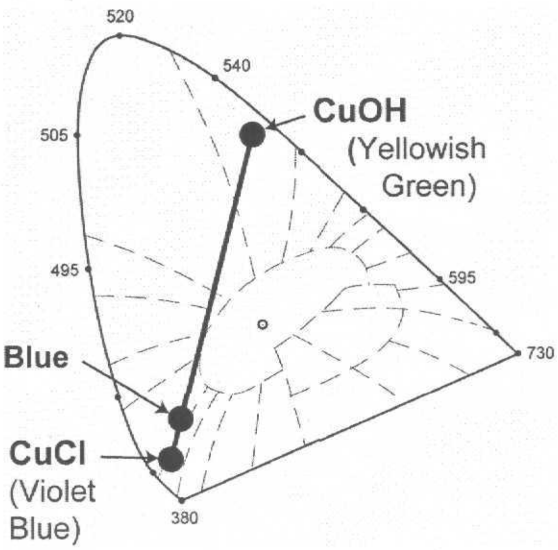


BLUE FLAMES

- Copper is not in the same chemical group as strontium; however, it follows similar color chemistry. The two color species are:

CuCl → Violet blue (~450 nm)

CuOH → Yellowish green (~540 nm)



- One might think that CuOH should be totally avoided. However, a small amount should act to improve the color by shifting the color point from violet blue to blue with only a little loss of purity.

YELLOW FLAMES

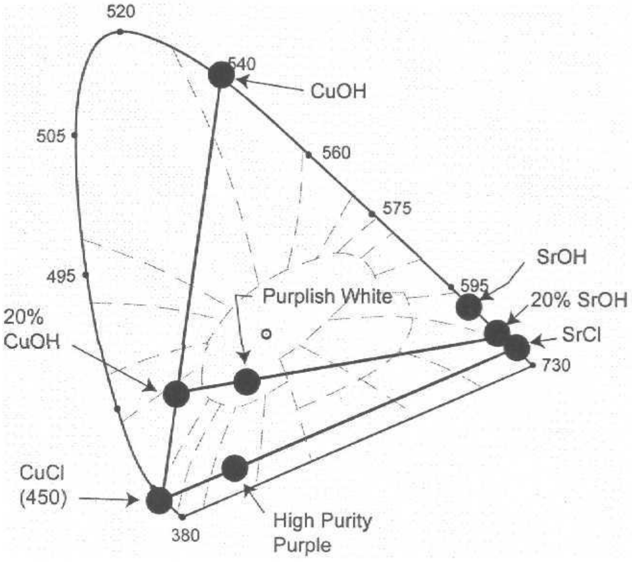
- Sodium is a very strong atomic emitter of yellow light. Thus, the use of a sodium salt is about all that is necessary to produce a fairly good yellow flame. None of the subtleties of other colored flame production are necessary (e.g., color enhancers, flame temperature, etc.).

- However, there are two factors that make sodium yellow flames less than trivial.
  - Many sodium compounds are hygroscopic.
    - = Na_3AlF_6 — good
    - = $Na_2C_2O_4$ — ok
    - = $NaNO_3$ & $NaClO_3$ — poor
  - The use of water soluble sodium color agents and magnesium or magnalium can lead to adverse reactions, which can cause dangerous heating of damp mixtures.

- The solution to both of these problems is the use of non-aqueous binders or non-soluble sodium salts, such as cryolite (Na_3AlF_6).

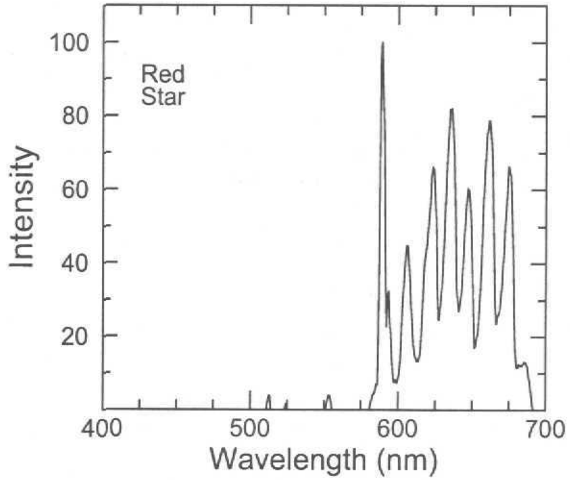
PURPLE FLAME

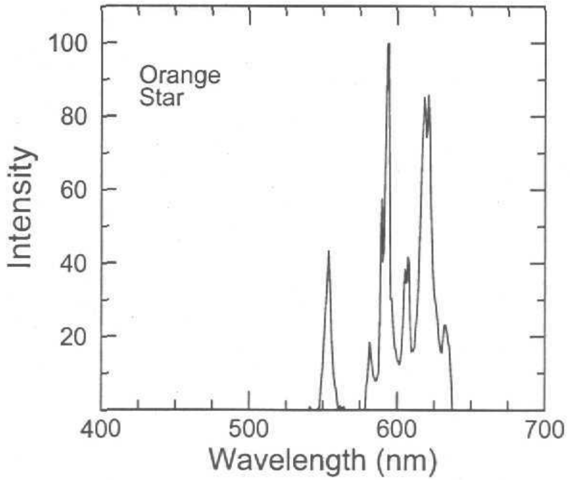
- **High quality purple can be produced using a combination of SrCl and CuCl. However, the presence of about 20% SrOH and CuOH will drastically reduce the purity of the purple flame.**



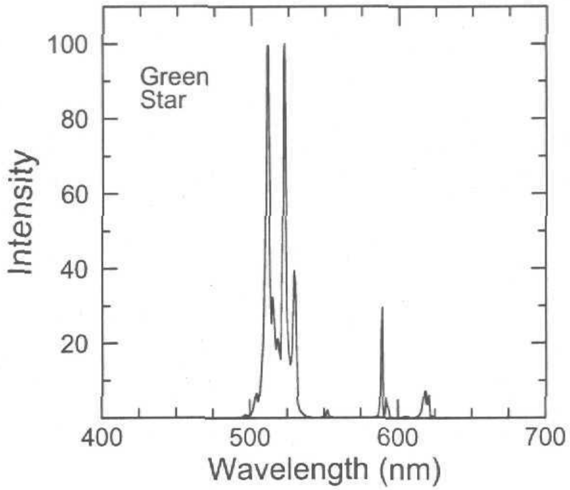
- **Thus hydrogen rich fuels should be avoided in purple flames. Metal fuels and charcoal would be desirable fuels, and Dechlorane should be desirable as a chlorine donor. Douda suggested that high flame temperatures might be useful because mono-hydroxides are probably less temperature stable than monochlorides.**

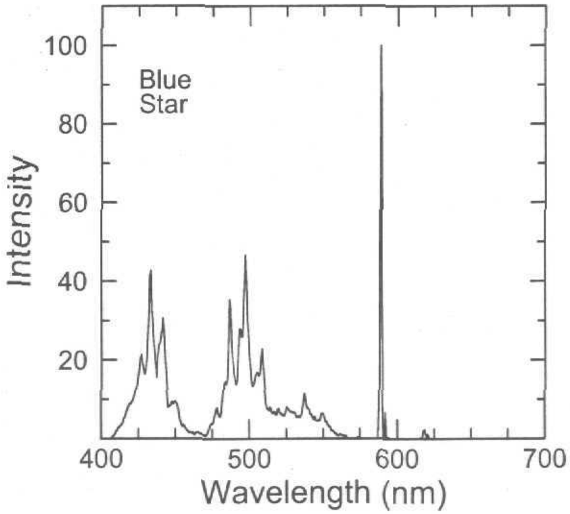
EXAMPLES OF SPECTRA FROM TEST STARS



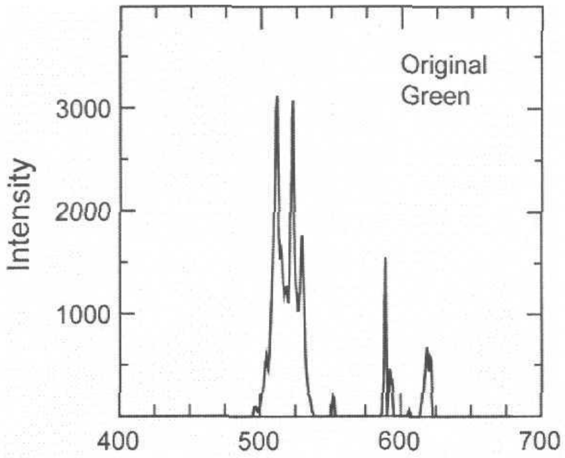


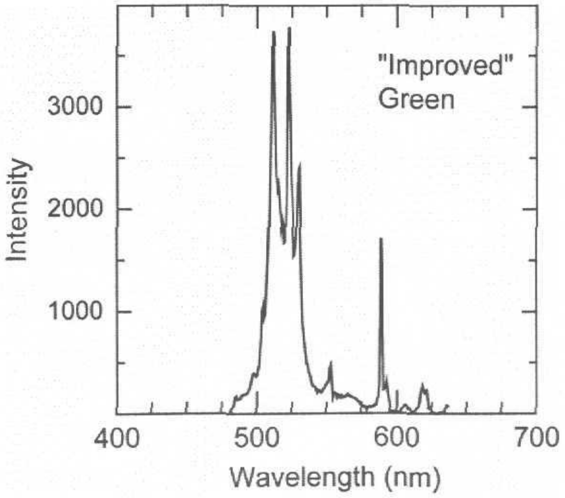
EXAMPLES OF SPECTRA FROM TEST STARS (Cont.)





COMPARISON OF SPECTRA FROM 2 GREEN STARS





IDENTIFICATION OF MAJOR SPECTRAL FEATURES BY CHEMICAL SPECIES AND BAND GROUP.

Source (a)	**Wavelength (nm)** (b)	**Relative Intensity** (c)
SrCl	**689**	**<1**
	674 – 676 (d)	**5**
	661 – 662 (d)	**10**
	649	**4**
	636	**10**
	624	**2**
SrOH	**608 – 611** (d)	**10**
Sr (e)	**461**	**10**
CaCl	**633 – 635** (d)	**1**
	621 – 622 (d)	**10**
	618 – 619 (d)	**10**
	605 – 608 (d)	**1**
	593	**10**
	581	**4**
CaOH	**644**	**2**
	622	**10**
	602	**2**
	554	**5**
Ca (e)	**442 – 445** (d)	**10**
Na	**589**	**10**

MAJOR SPECTRAL FEATURES (Continued)

Source (a)	**Wavelength (nm)** (b)	**Relative Intensity** (c)
BaCl	**532**	**3**
	524	**10**
	521	**1**
	517	**2**
	514	**10**
	507	**1**
BaOH	**513**	**10**
	488	**8**
Ba (e)	**554**	**10**
CuCl (f, g)	**538**	**2**
	526	**4**
	515	**2**
	498	**4**
	488	**8**
	479	**5**
	451	**1**
	443	**6**
	435	**9**
	428	**7**
	421	**4**
CuOH	**537**	**10**
	530	**9**
	524	**9**
	505	**6**
	493	**5**
Cu (e)	**522** (d)	**10**

TABLE NOTES

(a) These data are taken from Pearse and Gaydon, or Herrmann and Alkemade.

(b) Wavelengths are only reported to the nearest nm.

(c) The reported relative intensities are normalized to 10 for the strongest emission within a group of features from each chemical species. Different band groups for the same chemical species are separated by a single solid line in the table. Because intensities are normalized within each group and because the manner of excitation for the spectra in the literature is generally different than that for pyrotechnic flames, it cannot be assumed that the intensities listed in the table will be those observed in pyrotechnic flames.

(d) When two or more spectral features are within about 2 nm of each other, they are listed as a single feature showing a *range of wavelengths and with the combined intensity of* the features.

(e) Other weaker atomic lines occurring in the visible range are not reported.

(f) Pearse and Gaydon report six groups of bands for CuCl; however, the bands in only three of the groups were seen in flame spectra examined for this article. Also they appear to have collectively normalized the intensities of the bands (i.e., the strongest band in each group is not set to 10).

(g) Shimizu reports a total of 31 bands for CuCl, only the 10 strongest of those correspond to wavelengths reported by Pearse and Gaydon.

THE USE OF POTASSIUM OXIDIZERS

- ***Potassium oxidizers (perchlorate and chlorate) are*** **often used for colored flames because:**
  - **They only produce weak violet emissions in the visible spectrum. Thus color purity is not seriously reduced.**
  - **They act as ionization buffers, thereby promoting the production of desirable color species.**

$$\mathrm{K + heat} \leftrightarrow \mathrm{K^{+} + e^{-}}$$

$$\mathrm{2\,e^{-} + Sr^{2+}} \leftrightarrow \mathrm{Sr_{(g)}}$$

$$\mathrm{Sr_{(g)} + Cl} \leftrightarrow \mathrm{SrCl_{(g)}}$$

  - **They have other desirable properties.**

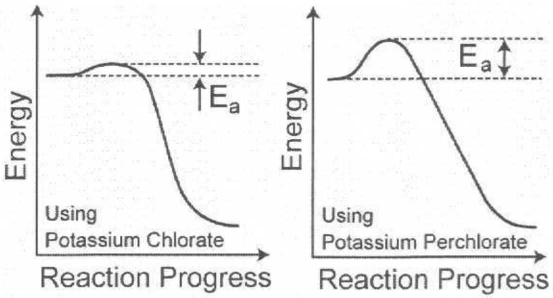
= Non-hygroscopic.

= Inexpensive.

THE USE OF CHLORATE OXIDIZERS

- Until recently, potassium chlorate and barium chlorate were used extensively. Good colors were produced using relatively inexpensive formulations that were easy to ignite.

- The ease of ignition of compositions using chlorate oxidizers is the result of low activation energy barriers.



- The low activation energy barrier for compositions using chlorate oxidizers has contributed to manufacturing accidents.

- Approximate sensitivity of chlorate compositions:

  Potassium < Barium < Sodium < Ammonium

  [Fairly Sensitive] ➔➔➔ [Spontaneously Explodes]

METAL FUELS FOR COLORED FLAMES — SAFETY

- Metal fuels are used to raise flame temperatures by producing more thermal energy than most other fuels. Generally the only metals used for this are magnesium, magnalium (Mg/Al) and aluminum.

- For safety reasons (accidental ignitions and violent reactions), metal fuel particle size should be no finer than is required for their complete consumption in the flame. Also, it is less expensive.

- An oxide coating forms on the surface of aluminum particles, which tends to protect it against chemical action. This oxide layer is also formed on magnalium, but is less protective. (In alloys of less than 30% aluminum, the oxide coating's effectiveness has been significantly reduced.) In terms of safety:

Safety:

Al > Mg/Al > Mg

METAL FUELS FOR COLOR FLAMES — EASE OF USE

- Because of the absence of a naturally formed protective layer on the surface of magnesium particles, it is necessary to take special measures.
  - Use non-aqueous binding:
    - Nitrocellulose with acetone.
    - Parlon with acetone plus MEK.
    - Red gum or shellac with dry alcohol.
  - Apply protective coating to magnesium particles [Shimizu; Alenfelt].
    - Treatment with $K_2Cr_2O_7$.
    - Treatment with NH_4VO_3, $(NH_4)_6Mo_7O_{24}$, and $NH_4H_2PO_4$.
    - Treatment with boiled linseed oil.
- Thus in terms of ease of use:

Ease of Use:

Al > Mg/Al > Mg

METAL FUELS FOR COLORED FLAMES — COLOR PURITY

- When metals are burned, they form oxides (Al_2O_3 and MgO) that may weaken the purity of flame color. This is because their boiling points are so high that they remain as liquid droplets and thus emit a continuous (white light) spectrum.

Al_2O_3	Boiling point = 2980 °C
MgO	Boiling point = 3600 °C

- If there is a source of Cl_2 in the flame, magnesium oxide will react to form magnesium chloride, which has a relatively low boiling point.

$$MgO + Cl_2 \rightarrow MgCl_2 + O$$

$MgCl_2$ Boiling point = 1412 °C

- The same reaction does not occur for aluminum oxide; thus in terms of color purity, magnesium is best!

Color Purity:

Mg > Mg/Al > Al

FLAME DEOXIDIZING AGENTS

- In a flame, near the limits of its envelope, there is a tendency to acquire oxygen from the air and for undesirable color producing oxides to form.

$2\ SrCl_{(g)} + O_2 \leftrightarrow 2\ SrO_{(g)} + Cl_2$ (Orange)

$2\ BaCl_{(g)} + O_2 \leftrightarrow 2\ BaO_{(g)} + Cl_2$ (Yellow)

$2\ CuCl_{(g)} + O_2 \leftrightarrow 2\ CuO_{(g)} + Cl_2$ (Red)

- The effect is to have flame tips that have lost the desired color and thus lower the purity of the color as seen at a distance.
- Fish suggested the use of a low reactivity fuel ("flame deoxidizing agent") to help counter this effect. Near the burning surface, this fuel competes poorly for pyrotechnic oxygen. However, it may react near the flame tips, keeping that area oxygen deficient, and thus reduce undesirable oxide formation. Some flame deoxidizing agents:

Hexamine
Sulfur
Asphaltum
Stearic acid
Para-dichlorobenzene
Graphite

STAR BURNING CONSIDERATIONS

- In addition to developing a color star formulation that produces excellent color, it is important that the color star has good ignition characteristics and an acceptable burn rate.
  - Chlorine donors resulting in relatively easy ignition are:
    = Saran resin
    = Parlon
  - Fuel's ease of ignition when using $KClO_4$:

= Charcoal	Difficult
= Metals	Difficult
= Red gum	Easy
= Sulfur	Easy (but not safe)

  - Slow burning compositions are often found when using NH_4ClO_4 as the sole oxidizer. (Except when Cu compounds are used that catalyze the reaction.)

ADDITIONAL FORMULATIONS:

Color Star Formulations [Veline] **are given in CERL Training 06.**

Color Lance Formulations [Kosanke]:

Table 1. Primary Color Lance and Lance Prime Formulations.

Ingredient	Red Star	Red Lance	Green Lance	Blue Lance	Lance Prime
Ammonium perchlorate	31	37	37	39	—
Potassium perchlorate	31	10	10	15	58
Red gum (Accroides)	15	8	8	3	6
Hexamine	—	8	8	5	—
Strontium nitrate	—	30	—	—	—
Strontium carbonate	23	7	—	—	—
Barium nitrate	—	—	37	14	—
Manganese dioxide	—	—	—	3	—
Rice starch	—	—	—	6	—
Paris green (a)	—	—	—	5	—
Copper metal	—	—	—	10	—
Silicon (325 mesh)	—	—	—	—	12
Titanium (325 mesh)	—	—	—	—	12
Charcoal (air float)	—	—	—	—	12
Burn Rate (sec/inch)	—	25	23	24	—

(a) Paris green is actually copper-acetoarsenite.

Table 2. Composite Color Lance Formulations.

Composition	Yellow	Orange	Chartreuse	White	Purple	Aqua
Red lance comp.	25	60	14	14	60	—
Blue lance comp.	—	—	—	28	40	25
Green lance comp.	75	40	86	58	—	75
Burn Rate (sec/inch)	24	—	—	—	25	—

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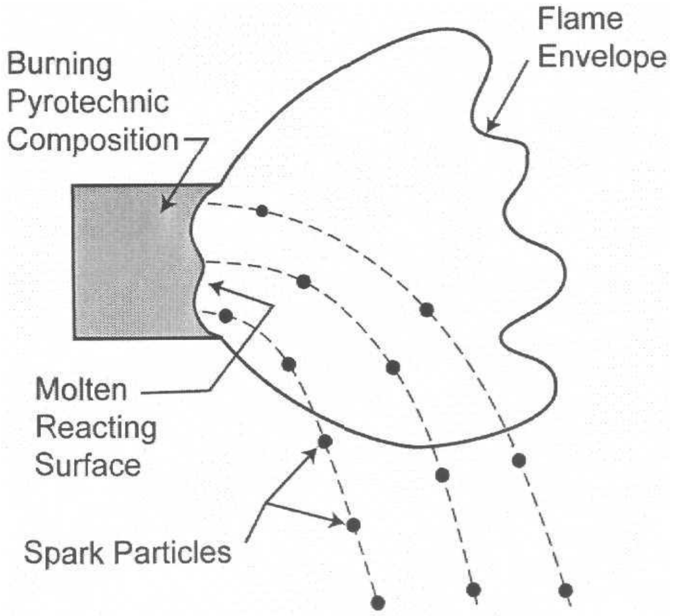
SECTION 8

CHEMISTRY OF SPARKS, GLITTER AND STROBE

- **Sparks and Incandescent Light Emission**
- **Control of Spark Duration**
- **Firefly Effect and Branching Sparks**
- **Basic Glitter Chemistry**
- ***Control of Glitter***
- **Pyrotechnic Strobe Effect**

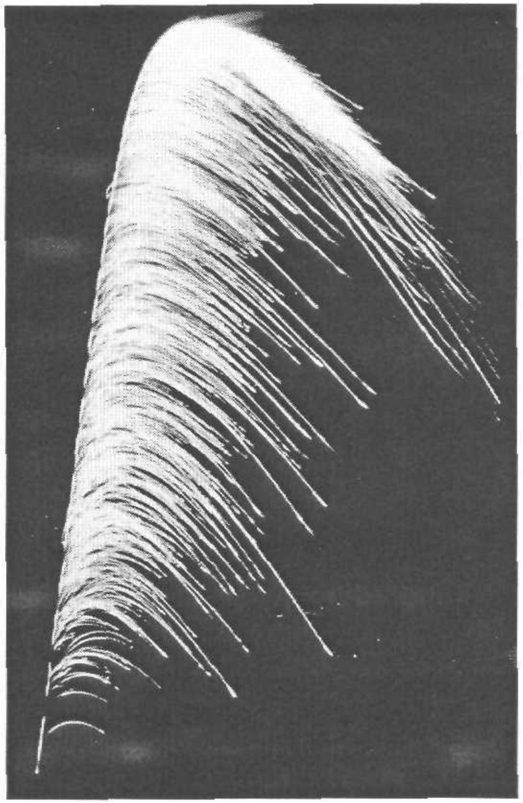
SPARKS ARE INCANDESCENT PARTICLES

- **When solid or liquid (molten) particles are heated to high temperature, they incandesce (glow) like the filament of a light bulb.**
- **Pyrotechnically generated sparks are solid or liquid particles ejected from the burning surface, and which have been heated to high temperature by the chemical reactions and flame.**



SIMPLE SPARK EXAMPLE

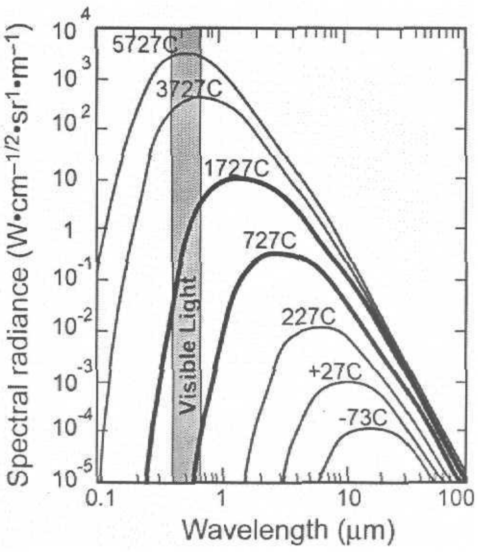
- Whitish sparks produced by a comet containing titanium particles.



LIGHT INTENSITY FROM “BLACK BODIES”

- Black bodies are ideal incandescent objects; they are perfect emitters (and absorbers) of light. The behavior of pyrotechnic spark particles approximates that of black bodies.

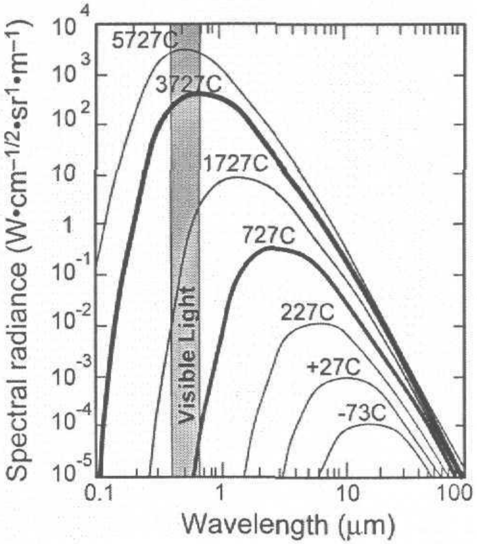
- Light intensity from black bodies increases radically as a function of temperature.



- Between about 700 and 1700 °C, the intensity of a black body increases by about a factor of 30 overall and by a factor of about 100,000 in the visible region.

PERCEIVED COLOR OF BLACK BODIES

- **At about 700 °C most of the emissions from a black body are in the infrared region. However, some of the light falls in the extreme long wavelength end of the visible region, thus appearing dim red.**

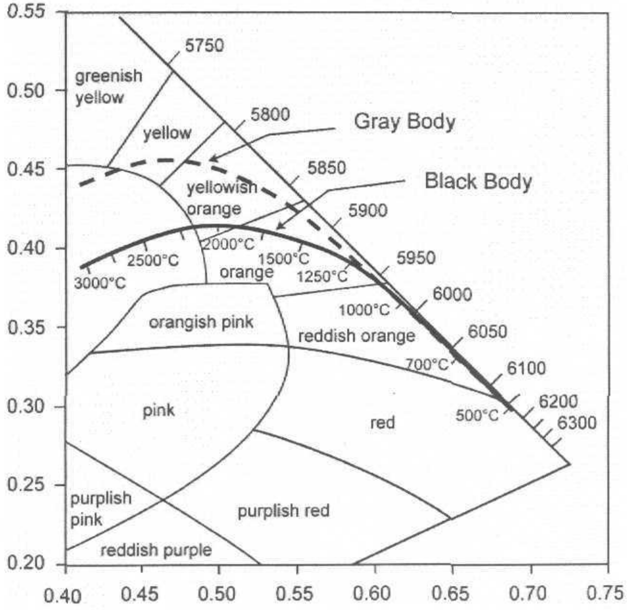


- **At about 3700 °C the peak black body emissions are in the visible region and are more evenly distributed, thus appearing bright white.**

COLOR OF BLACK BODIES AND "GRAY" BODIES

- **Gray bodies are loosely defined as less than perfect black bodies. The behavior of pyrotechnic sparks falls roughly in the range between that shown below for black bodies and gray bodies.**

- **The colors produced by black bodies and gray bodies, as a function of temperature, range from red to white as shown [Shimizu]:**



APPEARANCE OF PYROTECHNIC SPARKS

- **The color and brightness of sparks are inextricably locked together. For example, dim red and bright white sparks are possible, whereas bright red and dim white sparks are impossible.**

Temperature °C	Descriptive Color	Relative Brightness*
500	Red	1
850	Reddish orange	4
1500	Orange	7
2200	Yellow to yellowish white	9
3000	White	10

* Note that brightness is a subjective (mental) response to a visual stimulus. Brightness, for points of light against a dark background, is approximately a logarithmic response to light intensity.

SPARK PRODUCING GERB FORMULATIONS

- **Sparks are probably the oldest pyrotechnically produced effect and can be generated using a wide variety of materials.**

Gerb Formulations from Kentish (1905)

	Kentish Formulation Number											
Ingredient	1	2	3	4	5	6	7	8	9	10	11	12
Sulphur	2	3	—	1	—	2	3	2	2	2	—	—
Nitre*	2	2	—	—	—	10	6	4	9	4	—	—
Mealpowder	16	36	4	8	16	—	9	16	2	2	8	3
Steel Filings	1	6	—	—	—	—	—	—	—	—	—	—
Cast Iron Borings	5	8	1	3	8	7	5	8	5	3	—	—
Charcoal	—	—	—	—	1	2	2	1	2	2	—	—
Coke Grains	—	—	—	—	—	—	—	—	—	—	1	—
Porcelain Grains	—	—	—	—	—	—	—	—	—	—	—	1

Nitre = Potassium nitrate

- **In principle, inert materials can be used to generate sparks, but in practice, this is not effective.**

SPARK REACTION WITH AIR OXYGEN

- Inert spark particles ejected from a flame may initially glow brightly, but they rapidly cool becoming dim and then invisible. Aesthetically such rapidly dying sparks are quite unattractive.

- For sparks to remain bright for a longer time, they must continue to react and produce heat energy as they fall through the air. This spark reaction is oxidation, with the spark particle as the fuel and air oxygen as the oxidizer, for example:

$$C_{\text{(high temp.)}} + O_2 \rightarrow CO_2 + \text{heat}$$

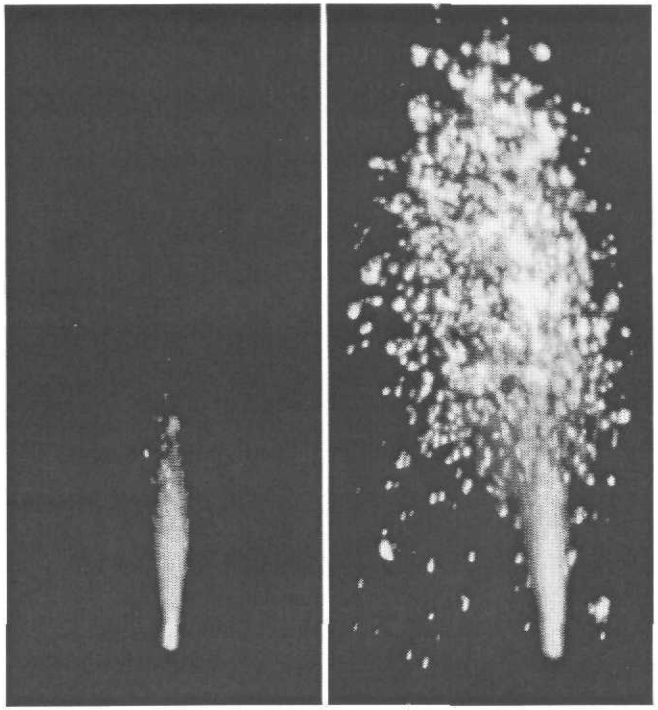
$$4\,Al_{\text{(high temp.)}} + 3\,O_2 \rightarrow 2\,Al_2O_3 + \text{heat}$$

$$Ti_{\text{(high temp.)}} + O_2 \rightarrow TiO_2 + \text{heat}$$

- For such reactions to occur, the spark particles must initially be raised above their ignition temperatures by the flame.

NON-REACTING SPARK EXAMPLE

- These are two identical iron fountains with the exception that the iron in the one on the left is in the form of stainless steel granules, which are resistant to air oxidation.



ELEMENTS COMMONLY USED FOR SPARK GENERATION

- Properties and spark colors:

Material	Electro-Negativity	Spark Color	Boiling Point (°C)
Carbon	2.5	Orange	4830
Iron	1.8	Yellow	2750
Aluminum	1.5	Pale yellow to white	2467
Titanium	1.5	Pale yellow to white	3287
Zirconium	1.4	White	3580
Magnesium	1.2	White	1090

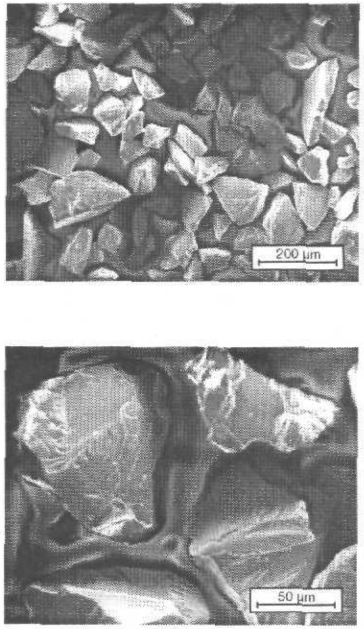
- Electronegativity is often a predictor of spark color.
  - This is because it is counter-indicative of the material's affinity for oxygen.
  - Thus materials with low electronegativity more readily combine with air oxygen, tending to raise the spark's temperature and shift its color toward white.

MELTING AND BOILING POINTS

- The temperatures at which phase changes take place for a spark material are important for two reasons.
  - It is only solids and liquids that incandesce. Therefore, if a spark material's boiling point is quite low it may be vaporized and lost as a spark.
    - = For example, magnesium's boiling point is only 1100 °C and is easily vaporized at temperatures well below the burning temperature of Black Powder.
  - Large amounts of energy are consumed in phase transitions, especially vaporization. Thus, melting and boiling points of metals and their oxides would be expected to set limits on temperatures attained during air oxidation of spark materials.

VIEWS OF MAGNALIUM PARTICLES

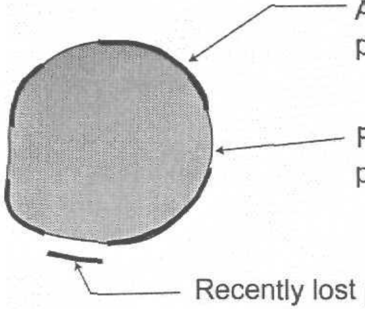
- Although magnalium is composed of two ductile metals, it is quite brittle. Note the "whiskers" and fracture patterns seen in the surfaces of these *particles*.



Whiskers and Fracture Patterns

CONTROL OF SPARK DURATION

- In many cases, the initial size of a particle determines its lifetime as a spark, with large particles generally persisting for a long time. However, if a spark *particle's exposed surface* is protected to some extent from air oxidation, its lifetime will be extended.
- In some cases, the oxidation products of the particle itself may provide some protection. For example, the accumulation of oxides on the surface of Fe, Al and Ti particles probably act to slow their air oxidation.



Areas of heavy oxide protecting surface

Rapid air oxidation taking place on exposed surface

Recently lost portion of heavy oxide coating

- However, in a given formulation, it is primarily particle size that determines a metal spark's duration.

DEALING WITH CORROSION

- When some metals are in contact with oxidizers, they can be oxidized (corroded) in a matter of days. As a result, their ability to produce attractive sparks can be lost. In these cases it is necessary to control this undesirable oxidation.
  - Traditional Method:
    - = Coat iron or magnesium with linseed oil.
  - Alternative:
    - = Non-aqueous binding (preferable in compositions with magnesium).
- Example:

Ingredient	
Handmade meal powder	65
Iron (coarse)	25
Aluminum (40 mesh, flake)	5
Shellac	5

Dampen composition with alcohol.

CONTROL OF CHARCOAL SPARK DURATION

- In the case of charcoal particles, the oxide being produced is a gas (CO_2), which provides no air oxidation protection for charcoal spark particles.
- Long lasting carbon sparks are the result of protection provided by the chemically inert combustion products of a Black Powder star composition (i.e., K_2CO_3 and K_2SO_4).
  - Black Powder burning produces potassium carbonate and potassium sulfide (simplified chemical equation):

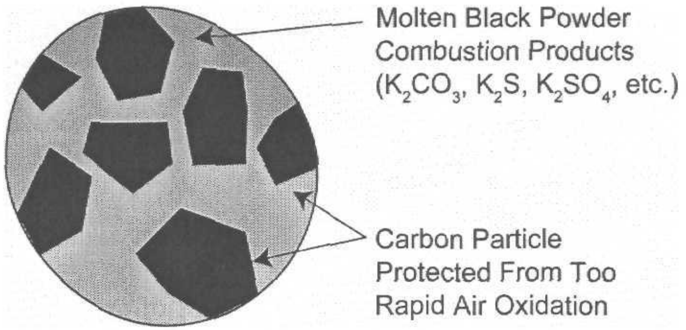
$$8\ KNO_3 + 11\ C + 2\ S \rightarrow 4\ N_2 + 9\ CO_2 + 2\ K_2CO_3 + 2\ K_2S + \text{heat}$$

  - The air oxidation of potassium sulfide produces potassium sulfate:

$$K_2S + 2\ O_2 \rightarrow K_2SO_4 + \text{heat}$$

CONTROL OF CHARCOAL SPARK DURATION (Continued)

- **The presence of molten Black Powder combustion products retards the air oxidation of the residual carbon particles.**



- **It *is likely* that the size of the *overall* charcoal *spark* particle plays a role in spark duration. Large particles have larger mass to surface area ratios, which should lead to longer duration sparks.**

- **Charcoal particle size plays a role in determining *spark duration; however, more important* is the amount of molten combustion products.**

CONTROL OF CHARCOAL SPARK DURATION (Continued)

- **When excess sulfur is present, the combustion products include potassium disulfide rather than potassium sulfide. This adds another energy producing air oxidation step to the production of potassium sulfate.**

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2 + \text{heat}$$

$$K_2S + 2\,O_2 \rightarrow K_2SO_4 + \text{heat}$$

- **The result is greater heat production and better protection for the charcoal particles (i.e., longer duration sparks).**

	Spark Duration	
	Long	Short
Ingredient	[Freeman]	[Shimizu]
Handmade meal powder	65	60
Charcoal (air float)	20	20
Dextrin	5	5
Handmade sulfurless meal powder	—	15
Sulfur	10	—
S/KNO_3 *ratio*	0.33	0.11

EFFECT OF REACTION RATE ON METAL SPARKS

- Oxidizer and fuel combinations that produce drossy residues can retard the air oxidation reaction rate of titanium sparks.

Ingredient	Yellow Sparks [Oglesby]	White Sparks [J-W]
Potassium nitrate	54	—
Potassium perchlorate	—	45
Titanium (10–20 mesh, flake)	16	20
Dextrin	4	5
Sulfur	13	—
Charcoal	13	—
Zircalium (Al_2Zr, –100 mesh)	—	20
Accroides resin	—	10

(J-W = Jennings-White)

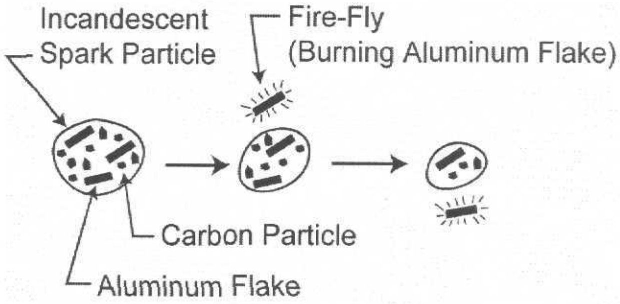
- Because the air oxidation rate is lower, the spark should last longer. It also appears yellowish, because its temperature is lower.

- Similar effects are seen with aluminum sparks [Shimizu].

FIREFLY SPARK EFFECT

- Firefly effects (also called transformation or transition effects) are long-duration sparks that appear to change from dim gold to bright silver.

- These sparks are composed of both carbon and aluminum particles in a dross droplet.

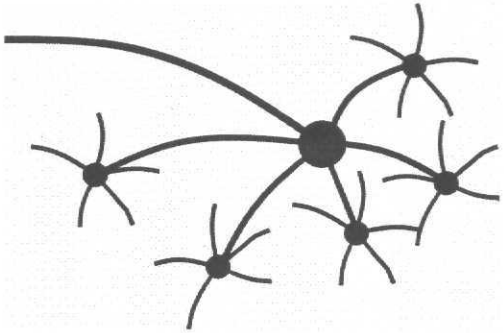


- At some point during the lifetime of the spark, burning aluminum particles at higher temperature (color and intensity) are thought to separate from the spark particle [Shimizu].

- Firefly effects are distinct from “flitter” effects, which are a persistent unchanging bright white metal spark effect typically produced using aluminum.

BRANCHING SPARKS

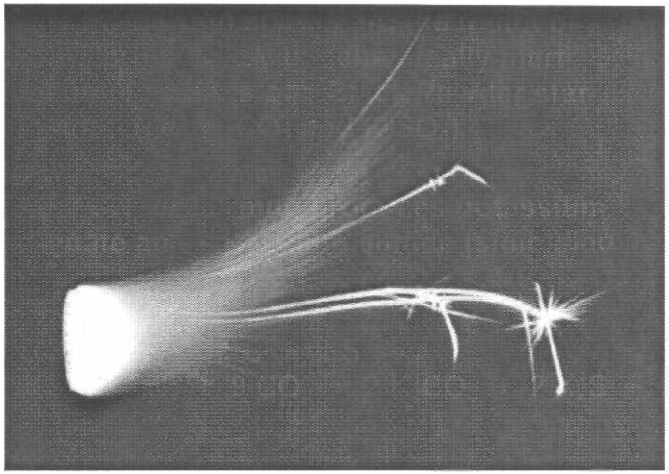
- Spark particles that branch are uniquely attractive when viewed from close range.



- Unfortunately, the physical/chemical mechanism of spark branching is not well understood.
- Probably the best sources of branching sparks are cast iron (Fe with ≈2% C) and the Senko-Hanabi reactions.
- Other metals produce some spark branching but not as often or as attractive.

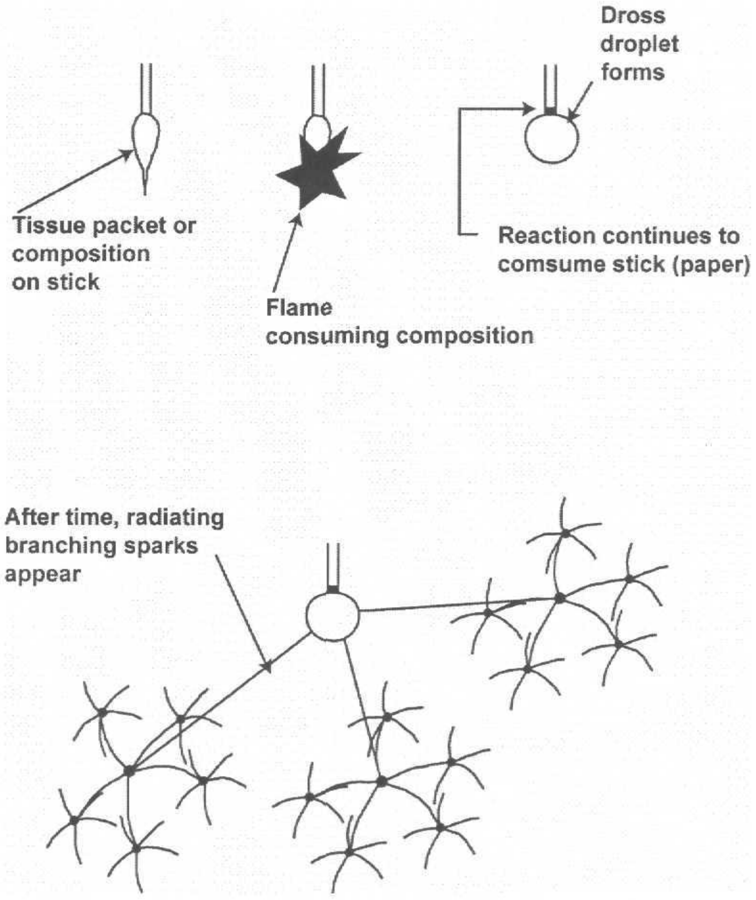
EXAMPLE OF FERROALUMINUM SPARK BRANCHING

- Branching sparks produced by introducing 20–40 mesh ferroaluminum particles into a gas burner flame.



SENKO-HANABI EFFECT

- Senko-Hanabi is a Japanese fireworks effect in which very delicate branching sparks are produced.



Dross droplet forms

Tissue packet or composition on stick

Reaction continues to comsume stick (paper)

Flame consuming composition

After time, radiating branching sparks appear

SENKO-HANABI CHEMISTRY

- There are two basic chemical reaction paths to the production of Senko-Hanabi's branching sparks, depending on the amount of sulfur present.
  - Type 1:

$$2\,KNO_3 + 3\,C + S \rightarrow K_2S + 3\,CO_2 + N_2$$

$$K_2S + 2\,O_2 \rightarrow K_2SO_4$$

  - Type 2 (more sulfur):

$$2\,KNO_3 + 3\,C + 2\,S \rightarrow K_2S_2 + 3\,CO_2 + N_2$$

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2$$

$$K_2S + 2\,O_2 \rightarrow K_2SO_4$$

- Unfortunately, the mechanism producing the branching sparks is not understood. However, the type of charcoal seems to be quite important.

SENKO-HANABI CHEMISTRY

- Senko-Hanabi chemistry is not completely understood; however, some things seem clear. When a Black Powder formulation is sulfur rich, potassium disulfide will be one of the products.

$$8\ KNO_3 + 11\ C + 4\ S \rightarrow 2\ K_2S_2 + 2\ K_2CO_3 + 4\ N_2 + 9\ CO_2$$

- If additional sulfur is present, more potassium disulfide can be formed through reaction with potassium carbonate [Shimizu].

$$2\ K_2CO_3 + 5\ S \rightarrow 2\ K_2S_2 + 2\ CO_2 + SO_2$$

- During the apparent quiescent period when the dross drop hangs glowing at the end of the straw, additional reactions produce heat and potassium sulfate.

$$K_2S_2 + O_2 \rightarrow K_2S + SO_2 + \text{heat}$$

$$K_2S + 2\ O_2 \rightarrow K_2SO_4 + \text{heat}$$

- The final branching spark producing step is not understood; however, it is well known that the type of charcoal used is important.

$$C + K_2SO_4 + (?) \rightarrow \text{Branching Sparks}$$

SPARKS AS AN AID TO IGNITION

- Gaseous reaction products tend to be relatively ineffective in causing ignition because they are low mass (light). This means that gaseous reaction products cannot be propelled far, are easily deflected, and carry little energy per unit volume.

- On the contrary, sparks (burning particles or molten dross) with their high mass are effective in causing ignition.

- Factors tending to produce sparks:
  - Large particle size, especially for fuels (not consumed)
  - High boiling point fuels (not consumed)
  - Air oxidizable fuels (more energy)
  - Sulfur and sulfides (dross)
  - Silicon (dross + energy)

SPARK AVOIDANCE

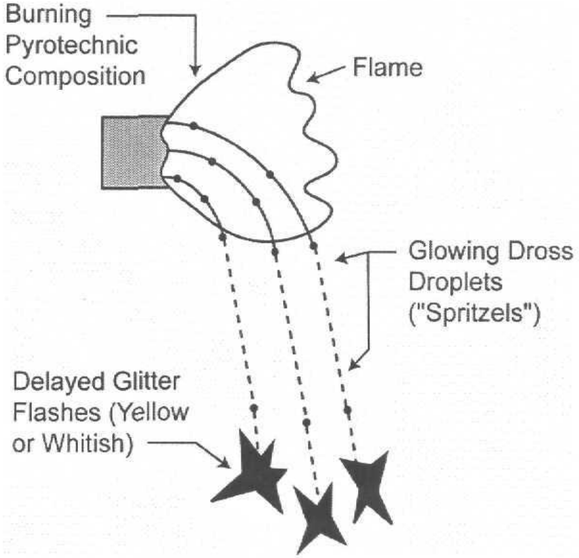
- There are times when spark production is undesirable. For example, in signal flares the production of sparks is a visual distraction, and the wasted energy means less light output is produced for a given weight of composition.

- Generally spark production can be avoided by doing the reverse of those thins that help produce sparks. Factors tending to eliminate sparks:

  - Small particles (consumed in the flame)
  - Low boiling point fuels (consumed in the flame)
  - Gas producing oxidizers, like NH_4ClO_4
  - Gas producing fuels, like hexamine

PYROTECHNIC GLITTER

- There are similarities between charcoal sparks and glitter, but the important difference is the delayed flash reaction, which produces the "glittering" effect.



- In contrast, note that the so-called "flitter" effect is one of continuous bright silver sparks, usually produced by aluminum.

GLITTER FOUNTAIN EXAMPLE

- Most glitter effects are seen as fireworks stars or comets. The drossy residues produced by burning glitter compositions makes fountain effects difficult, but not impossible to produce.

(Photo courtesy of R. Winokur)

GLITTER VS CHARCOAL SPARK FORMULATIONS

- There are similarities between these formulations.

Ingredient	Golden Streamer [Freeman]	Pearl Glitter [Oglesby]
Handmade meal powder	65	65
Sulfur	10	10
Dextrin	5	5
Charcoal (air float)	20	—
Barium nitrate	—	10
Aluminum	—	10

- One might correctly guess that the first formulation would produce gold sparks because of the abundance of charcoal.

- One might guess that the second would produce silver sparks from the aluminum. However, the second formulation produces a glitter effect.

- Generally preferred characteristics for glitter are:
  1) a long delay, before the appearance of
  2) bright flashes.

THEORIES OF GLITTER CHEMISTRY

- Theories for the production of glitter effects have been proposed by Fish, Oglesby and Stanbridge. All are credible and there is some basis for believing each of them. However, for brevity, only the one suggested by Oglesby will be discussed in detail. Following this discussion the three theories will be compared.

- To better follow the chemistry, it is useful to consider separately the reactions taking place:
  - In the reacting layer of the glitter star, are the "on board" reactions.
  - In the falling dross droplets (termed spritzels [Oglesby]), are the "spritzel" reactions.
  - Finally, the more violent flash is produced as the "flash" reaction.

OGLESBY'S GLITTER CHEMISTRY

- Note that the aluminum does not participate in the "on board" and "spritzel" reactions. Thus, for simplicity, it will not be expressly shown in the following chemical equations.

- The "on board" reaction produces K_2S_2:

1) $2\ KNO_3 + 3\ C + 2\ S \rightarrow K_2S_2 + 3\ CO_2 + N_2 + \text{Heat}$

- The "spritzel" reactions convert K_2S_2 to K_2SO_4:

2) $K_2S_2 + O_2 \rightarrow K_2S + SO_2 + \text{Heat}$

3) $K_2S + 2\ O_2 \rightarrow K_2SO_4 + \text{Heat}$

- The "flash" reaction produces much energy as K_2SO_4, a high temperature oxidizer, reacts with aluminum:

4) $3\ K_2SO_4 + 8\ Al \rightarrow 3\ K_2S + 4\ Al_2O_3 + \text{Heat}$

THE ROLE OF BARIUM NITRATE [OGLESBY]

- **The usefulness of barium nitrate in glitter may be explained by the following:**

1) $Ba(NO_3)_2 + 3\,C + S \rightarrow BaS + 3\,CO_2 + N_2 + \text{Heat}$ (on board reaction)

2) $BaS + 2\,O_2 \rightarrow BaSO_4 + \text{Heat}$ (spritzel reaction)

3) $3\,BaSO_4 + 8\,Al \rightarrow 3\,BaS + 4\,Al_2O_3 + \text{Heat}$ (flash reaction)

- **Note that:**

Spritzel temperature is probably about 1200 °C.

$BaSO_4$ (m.p. 1580 °C) solid at spritzel temp.

K_2SO_4 (m.p. 1069 °C) liquid at spritzel temp.

- **Because $BaSO_4$ is a solid, a greater proportion of sulfate can form prior to the flash reaction. This results in a <u>longer delay</u>, as well as more oxidizer for the flash reaction (causing <u>bigger and brighter flashes</u>).**

THE ROLE OF ANTIMONY SULFIDE [OGLESBY/JENNINGS-WHITE]

- **Consider the following glitter formulation:**

Ingredient	%
Handmade meal powder	75
Aluminum	10
Antimony sulfide	10
Dextrin	5

- **In this formulation, there is a relative deficiency of elemental sulfur. Thus the likely "on board" reactions are:**

1) $2\,KNO_3 + 3\,C + S \rightarrow K_2S + 3\,CO_2 + N_2 + \text{Heat}$

2) $3\,K_2S + Sb_2S_3 \rightarrow 2\,K_3SbS_3 + \text{Heat}$

- **There is also the additional "spritzel" reaction to produce K_2S_2:**

3) $4\,K_3SbS_3 + 3\,O_2 \rightarrow 6\,K_2S_2 + 2\,Sb_2O_3$

THE ROLE OF ANTIMONY SULFIDE (Continued)

- The remaining reactions are the same as discussed earlier.
  - Further "spritzel" reactions:

    4) $K_2S_2 + O_2 \rightarrow K_2S + SO_2$ + Heat

    5) $K_2S + 2\,O_2 \rightarrow K_2SO_4$ + Heat
  - "Flash" reaction:

    6) $3\,K_2SO_4 + 8\,Al \rightarrow 3\,K_2S + 4\,Al_2O_3$ + Heat
- Because of the additional spritzel reaction step, (on the preceding page) there is additional delay in the onset of the flash reaction. This results in a more attractive glitter effect.

THE ROLE OF CARBONATES AND OXALATES

- Other materials are useful in delaying the production of sulfates for the flash reaction.

	Oxalate	Carbonate	Bicarbonate
Barium	X	X	
Strontium	X	X	
Magnesium	X	X	
Lithium	X	X	
Sodium	X		X
Potassium	X		X
Antimony	X		

X = Useful Materials

- Consider strontium oxalate as an example of how these materials generally function.

  1) $SrC_2O_4 \rightarrow SrCO_3 + CO$ (Consumes heat)

  2) $SrCO_3 \rightarrow SrO + CO_2$ (Consumes heat)

  3) $2\,SrO + 3\,K_2S_2 \rightarrow 2\,SrS + 3\,K_2S + SO_2$ + Heat

  4) $SrS + 2\,O_2 \rightarrow SrSO_4$ + Heat (Flash oxidizer)
  (m.p. 1605 °C)

WATER REACTIVITIES OF METALS WITH GLITTER ADDITIVES

- With some combinations of materials there is a potential for unwanted reactions to occur in moist compositions.

	Metal	
Ingredient	Aluminum	Magnalium
Lithium carbonate	**	
Sodium bicarbonate	**	
Lithium oxalate		**
Sodium oxalate		**
Antimony oxalate		**

** = Possible unwanted reaction upon dampening

- For example, lithium carbonate must not be used with aluminum; use lithium oxalate instead.

pH of saturated Li_2CO_3 solution = 11

pH of saturated $Li_2C_2O_4$ solution = 7

- Conversely, alkali metal oxalates (Li, Na, K, etc.) could cause problems with magnalium. Thus lithium carbonate and sodium bicarbonate are safer alternatives. (Reason is not understood.)

INFLUENCE OF METAL FUELS ON GLITTER

- The following statements generally summarize what is known:
  - Aluminum is a necessary component of glitter.
  - Certain alloys such as ferroaluminum and magnalium (with Al content > 30%) also function.
  - Certain other alloys such as zirconium-aluminum and zinc-aluminum do not function.
  - The principal characteristic effect of using magnalium is that apparently fewer spritzels are produced, but their subsequent flashes are bigger and brighter (louder, too).
  - Aluminum particle size and shape play a definite role in determining glitter performance. For example, spherical atomized particles seem to produce longer delays and larger flashes. Also, larger particles tend to produce whiter flashes, while smaller particles tend to produce yellower flashes especially if the composition contains a sodium salt.

COMPARISON OF GLITTER THEORIES

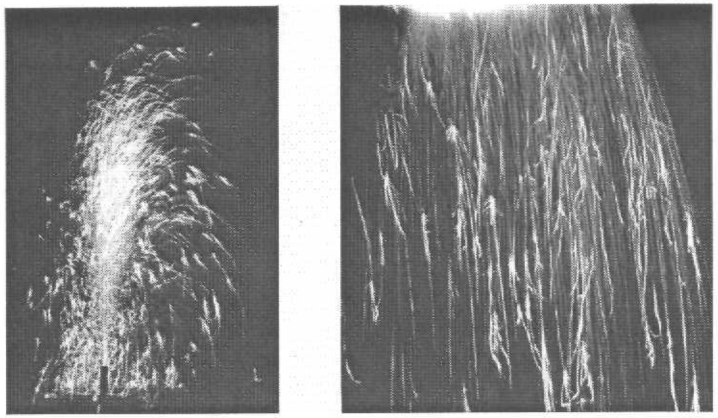
- Common elements:
  - The on board reaction produces some "starting materials".
  - The starting materials are modified as the spritzel falls through the air.
  - Finally, there is sufficient build-up of material to produce the flash reaction, which is primarily a reaction between potassium sulfate and an energetic fuel.
- Differences:
  - The main difference is only the energetic fuel of the flash reaction.
    - = Oglesby — Al
    - = Fish — Al_2S_3
    - = Stanbridge — Al_4C_3
- It is not necessary to know who is most correct to make good glitter; what is important is to understand how to control glitter delay.

CONTROL OF GLITTER DELAY

- Glitter = meal powder (or its components) + aluminum + delay agent(s)
- Delay agents (chemical delays):
  - Antimony sulfide alone.
  - Sulfur with at least some carbonate, oxalate, $Ba(NO_3)_2$, Fe_2O_3, etc.
  - Antimony sulfide + any other delay agent(s).
- Physical delays:
  - Poor incorporation (i.e., using handmade meal powder instead of commercial meal powder).
  - Larger metal fuel particle size.
- Generally, chemical influences play a greater role in providing delay than physical influences.

FERROALUMINUM SPARK EXAMPLES

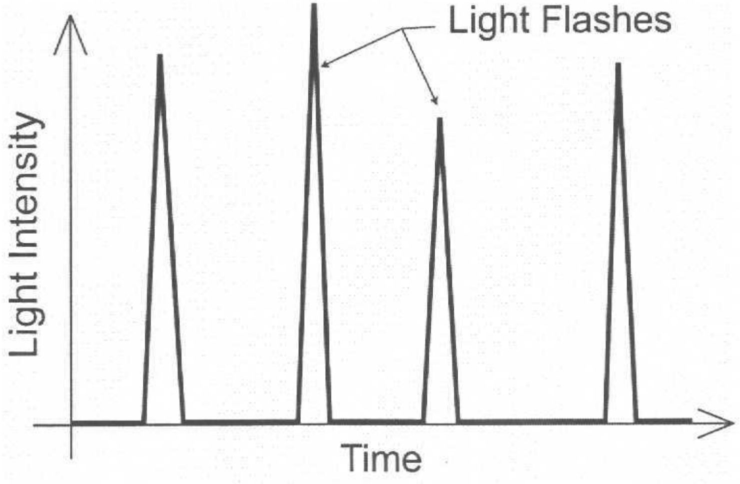
- **Some interesting delayed ignition sparks are produced with ferroaluminum (35:65) in simple rough powder formulations. These effects do not fit neatly in normal spark or glitter categories.**



PYROTECHNIC STROBE

- **Strobe effects are characterized by repeated flashes of light produced by a single pyrotechnic unit (for example, a star).**

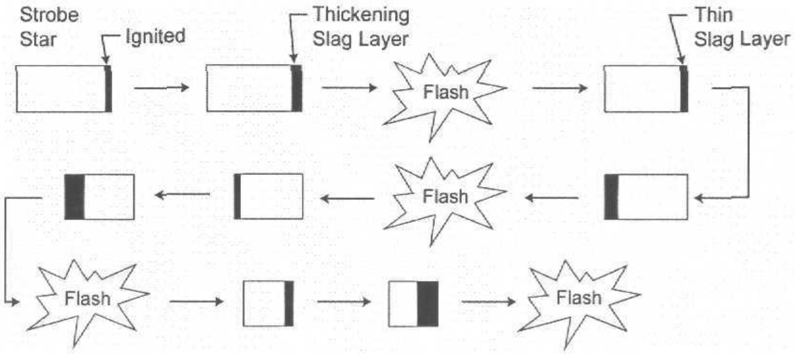
- **As a time sequence, a strobe star produces light as shown:**



- **There are repeated flashes of light, roughly equal in intensity, separated by more or less equal intervals of no light production.**

OBSERVATION OF STROBE

- Shimizu closely observed the burning of strobe stars and saw the following repeated series of events:
  - A dark or smolder reaction produces a growing slag layer with no light output.
  - Localized hot spots develop within the slag.
  - A violent (almost explosive) reaction of the slag produces a brilliant flash of light.



- Strobe can be seen as a continuing dark (smolder) reaction punctuated by flash reactions. Thus a strobe composition could be considered to be a combination of dark and flash mixtures.

DIVERSE STROBE FORMULATIONS

- There are many different formulations that are capable of strobing. Occasionally by looking for common elements, a mechanism can be discovered.

Ingredients	A	B	C	D	E	F	G	H	I	J	K
Barium nitrate	40	50									6
Sulfur	30										
Magnalium	14	20	33	30	25	20					17
Barium carbonate	10										6
Chlorowax	6										
Guanidine nitrate		30	33	42						70	8
Potassium perchlorate			33								
Ammonium perchlorate				28	60	50	60		50		51
Barium sulfate					15						9
Hexamine						30	40	50			
Lithium perchlorate								50			
Magnesium									50		
Mg_2Cu										30	
Parlon											3

A = Hyman (Green)
B = Schroeder
C, D, F, G, H, J = Jennings-White
E & I = Shimizu
K = Veline/Jennings-White (Green)

- Unfortunately, there are no readily apparent common elements to suggest the mechanism for strobe.

“DARK” AND FLASH BINARY MIXTURES

- Examples of known dark binary mixtures:

  Ammonium perchlorate with:
    - magnesium,
    - magnalium,
    - zinc,
    - copper,
    - cyanoguanidine, or
    - guanidine nitrate

  Sulfur with:
    - magnesium,
    - magnalium,
    - titanium,
    - copper, or
    - air

  Guanidine nitrate with:
    - ammonium perchlorate,
    - magnesium-copper alloy,
    - copper, or
    - copper(I) oxide

- Examples of known flash binary mixtures:

  Magnalium with:
    - barium nitrate,
    - barium sulfate,
    - ammonium perchlorate, or
    - potassium perchlorate

EXAMPLES OF STROBE COMPOSITIONS

- **For magnalium strobes, there is evidence that the magnesium content participates primarily in the dark reaction, and the aluminum content participates primarily in the flash reaction. Thus for the system:**

  NH_4ClO_4 / $BaSO_4$ / magnalium

  – Dark reaction: $NH_4ClO_4 + Mg \rightarrow$ products + heat

  – Flash reaction: $BaSO_4 + Al \rightarrow$ products + heat

  (Note that the flash reaction is the same as that postulated for certain glitters.)

  (Note that it has been reported that Mg/Al particles melt in two stages, first releasing Mg from the solid particle [Popov].)

- **For some strobe compositions without a metal fuel, the flash reaction appears to emanate from a molten phase that is formed during the dark reaction.**

CONTROL OF STROBE RATE

- **Changing the formulation can change the strobe rate in unpredictable ways. However, there are a few general rules.**

To increase strobe rate:

1. **Increase the percentage of metal powder in the formulation.**
2. **Decrease the particle size of the metal powder used.**
3. **Increase thermal feedback; for example by using box stars.**

To decrease strobe rate:

1, 2, 3 — The opposite of above.

- **Note that using too high a percentage of binder can cause a strobe formulation to burn continuously.**

ADDITIONAL FORMULATIONS

Shimizu's Magnalium Glitter (slightly modified by Jennings-White)

Handmade meal powder	65
Sulfur	15
Magnalium (50:50, -60 mesh)	10
Calcium carbonate	5
Dextrin	5

Comment:
This excellent glitter lies buried in Shimizu's glitter articles in *Pyrotechnica XIV*.

Jennings-White Magnalium Glitter (based on Winokur No. 14)

Handmade meal powder	68
Magnalium (20:80, 200 mesh)	8
Antimony sulfide	5
Dextrin	5
Sodium bicarbonate	5
Sulfur	5
Magnalium (10:90, 200 mesh)	4

Comment:
A magnalium glitter using unusual alloys.

Slow Magenta Strobe Pot (based on some Shimizu strobes)

Guanidine nitrate	55
Magnesium (-50 mesh)	18
Strontium sulfate	14
Parlon	5
Bismuth(III) oxide	4
Copper(II) oxide	4

Comment:
An example of ongoing research into color strobes. Shimizu uses lead oxide to generate hot spots in the dark reaction, thereby promoting the flash.

Shimizu's Firefly

Potassium nitrate	52	50
Sulfur	7	5
Charcoal	42	45
Aluminum (18–30 mesh, flake)	5	5
Starch	5	5
Barium sulfate	—	7

Comment
The type of charcoal plays an important role in achieving satisfactory results.

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SECTION 9

Pyrotechnic Smoke and Noise

- Physical Smoke
- Chemical Smoke
- Whistles
- Salutes / Reports

PYROTECHNIC SMOKE

- For the most part, vapors (gases) are not visible and do not appear as smoke or fog.
  - For example, water vapor is essentially invisible.
  - Clouds are tiny liquid water droplets (cumulus) or solid water particles (cirrus).
- Smoke is composed of tiny [≈0.0001 in.] solid or liquid particles dispersed in air. For example:
  - Theatrical smoke (organic liquid droplets).
  - Flash powder smoke (solid Al_2O_3 particles).
- There are two basic ways to produce smoke:
  - Physical smoke.
  - Chemical smoke.

PYROTECHNIC SMOKE TYPES

- **PHYSICAL SMOKE, particles are formed by vaporization and condensation of a solid (or liquid).**

SOLID (Large Particles) → **VAPOR** → **SOLID** (Small Dispersed Particles)

- **Examples:**
  - **Common colored smokes (dyes).**
  - **Theatrical smokes and fogs (organic liquid).**

- **CHEMICAL SMOKE, solid (or liquid) particles are formed as products of a chemical reaction.**

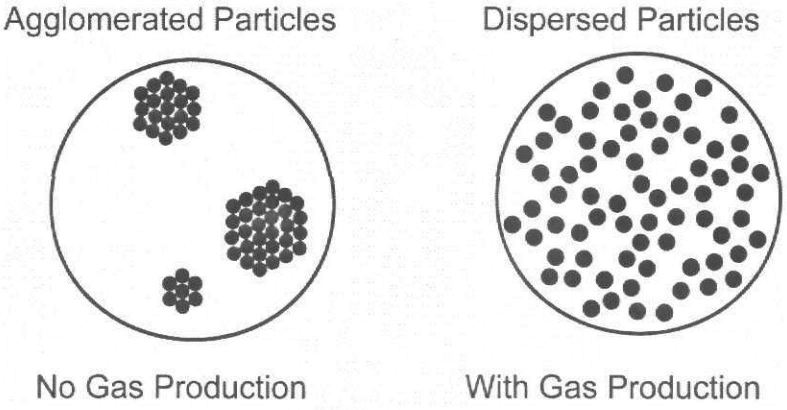
PYROTECHNIC COMPOSITION → **CHEMICAL REACTION** → **COMBUSTION PRODUCTS**

- **Examples:**
  - **Inorganic colored smokes.**
  - **Combustion by-products.**

PHYSICAL SMOKES

- **The pyrogen for smoke production is the pyrotechnic oxidizer plus fuel combination.**

- **The role of the pyrogen is two fold:**
  - **Provide the heat for vaporization of the smoke substance.**
  - **Produce gas to minimize agglomeration of smoke particles.**



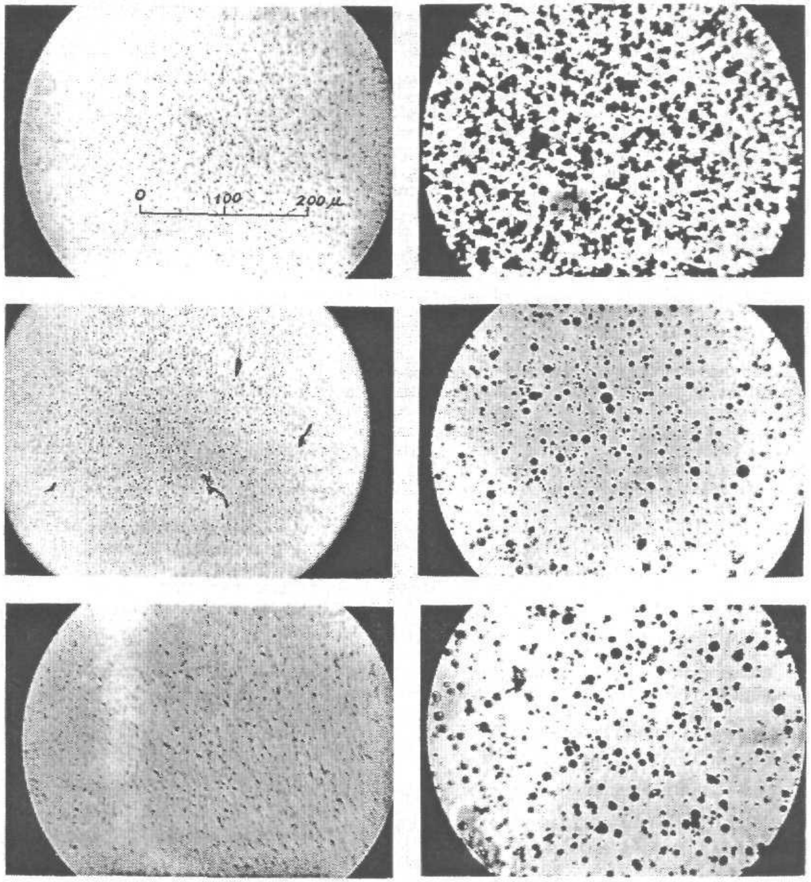
- **The effect of having dispersed particles is the appearance of a denser smoke cloud.**

PHYSICAL SMOKES (Continued)

- Effect of gas production on smoke particles

Smoke particles
(with gas production)

Volatilized Dye
(without gas production)



[Shimizu]

PHYSICAL SMOKES (Continued)

- The chemical reaction temperature must be low enough that the smoke substance is not destroyed (decomposed).
  - Colored smokes use dyes, which are complex organic molecules, as the smoke substance.
  - Most complex organic molecules decompose in the range of 100 – 300 °C.
  - Smoke dyes are resistant to thermal decomposition, but do decompose when temperatures exceed ≈300 °C. Thus, reaction temperature must be <300 °C.
- If the temperature of the pyrogen falls below its ignition temperature, it will be extinguished.
  - Thus the ignition temperature for the pyrogen must be significantly less than 300 °C.

IGNITION TEMPERATURES

- **Ignition temperature of common pyrotechnic mixtures** [Conkling and Shidlovskiy]:

Composition	T_i (°C)
– **Flash powder** [$KClO_4$ + Al]	≈750
– **Red star** [Mg + $Sr(NO_3)_2$ + $KClO_4$ + HCB + *asphaltum*]	≈500
– **Green star** [Mg + HCB + $Ba(NO_3)_2$]	≈450
– **Black Powder** [KNO_3 + charcoal + S]	≈350
– **H3 (break powder)** [$KClO_3$ + charcoal]	≈350
———— **Limit** —	≈300
– **$KClO_3$ + lactose**	≈200
– **$KClO_3$ + sulfur**	≈200

OPTIMUM SMOKE PYROGEN

- **Only chlorate oxidizers produce pyrogens with sufficiently low ignition temperatures for use with organic smoke dyes.**

- **Sulfur fuel with chlorate:**
  - **Has sensitivity problems [drop height ≈15 cm].**
  - **Produces SO_2 and Cl_2 gas (noxious).**

$$2\,KClO_3 + 2\,S \rightarrow K_2SO_4 + SO_2 + Cl_2$$

  - **Produces white smoke (SO_2 + H_2O).**

- **Lactose fuel with chlorate:**
  - **Only moderately sensitive [drop height ≈45 cm].**
  - **Produces abundant harmless gas (H_2O and CO_2).**

$$8\,KClO_3 + C_{12}H_{22}O_{11}\cdot H_2O \rightarrow 8\,KCl + 12\,CO_2 + 12\,H_2O$$

  - **Produces abundant thermal energy.**

MECHANISMS FOR LOWERING REACTION TEMPERATURE

- Low ignition temperatures do not mean that the flame (reaction) temperature will also be low.
- If the reaction temperature exceeds the decomposition temperature of the smoke dye, the dye will be destroyed.
- Mechanisms for lowering reaction temperature:
  - *Deviate from the stoichiometric oxidizer to fuel* ratio (≈2.7 : 1).
    - = Typical smoke ratio ≈1.4 : 1
  - Use a large amount of smoke dye.
    - = Vaporization of smoke dye consumes energy.
  - Add a thermal buffer.
    - = *$NaHCO_3$ — decomposes at 270 °C to produce CO_2* and consumes heat in the process.

SMOKE DYES AND TYPICAL FORMULATION

- Commonly used smoke dyes:

Rhodamine B	Red
Oil orange	Red
Aminoanthraquinone	Red
Oil scarlet	Red
Auramine	Yellow
Diparatoluidinoanthraquinone	Green
Phthalocyanine blue	Blue
Methylene blue	Blue
Indigo	Violet

(Caution, many dyes are suspected carcinogens.)

- Typical smoke formulation:

$KClO_3$	25
Lactose	20
Smoke dye	50
$NaHCO_3$	5 (adjustable)

INORGANIC PHYSICAL SMOKES

- **When the smoke substance is an inorganic material, generally there is little or no concern about its decomposition due to high reaction temperatures. However, in some cases high temperatures may cause the smoke substance to burn in air.**

- **Examples of inorganic physical smoke** [Lancaster]:

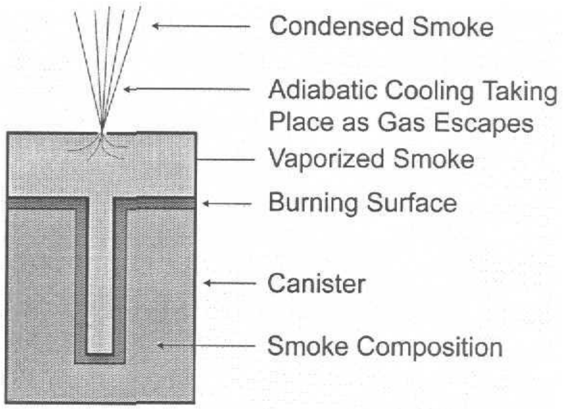
Ingredient	White Smoke	Yellow Smoke
Potassium nitrate	48.5	25
Sulfur	48.5	16
Arsenic sulfide	3.0	59

Note: The presence of SO_2 and As_2S_3 in these smokes makes them toxic.

- **In both cases, sulfur and arsenic sulfide, are partially consumed as fuel. However, the excess is vaporized and then condenses to form the smoke.**
  - **Note: The color of very small particles dispersed in air always appears lighter and whiter.**

SMOKE GENERATORS

- **To facilitate condensation of the smoke material, and to limit after-burning in air, it is useful to have the smoke exit the device at high pressure through a small hole. This results in a cooling of the gas stream as it expands to atmospheric pressure.**



Smoke Generator

- **The open space above the smoke composition allows the combustion products to cool somewhat before exiting.**

- **The open core increases the burning surface. It also aids the exiting of vaporized smoke dye without it being burned as it might if it had to pass through a large ash buildup from the pyrogen.**

CHEMICAL SMOKE

- **In chemical smokes, the smoke substance is a *product of the chemical reaction* and is not a component in the formulation.**

- **Black smoke example** [Shimizu]:

Ingredient	%
Potassium perchlorate	57
Sulfur	13
Anthracene	30

$$5\,KClO_4 + 5\,S + 2\,C_{14}H_{10} \rightarrow$$
$$5\,KCl + 5\,SO_2 + 10\,H_2O + 28\,C$$

- **In this case, the carbon produced by the reaction is the smoke substance. The sulfur dioxide and water vapor help keep the carbon particles from agglomerating.**

PYROTECHNIC SOUND

- **Although most pyrotechnic items produce some sound, *for whistles and salutes sound is the primary* effect.**

- **Modern formulations for whistle compositions and flash powders are not as sensitive to accidental *ignition as those from the past*. However, *once* ignited their potential for explosive output renders these materials worthy of great respect.**
  - **The quantity of unused composition must be kept as small as practical.**
  - **Finished items should be removed from the work area.**
  - ***Minimize* the input of thermal, mechanical and electrical energy to the compositions.**
  - **The use of chlorates, gallic acid, picrates, sulfur and sulfides should be avoided.**

WHISTLING SOUND

- Sound is a subjective response to nerve stimulus produced as the ear reacts to rapidly varying pressure.

- When the rapidly varying pressure is repetitive and in the range from about 20 to 15,000 Hz, the auditory response is to hear a tone.

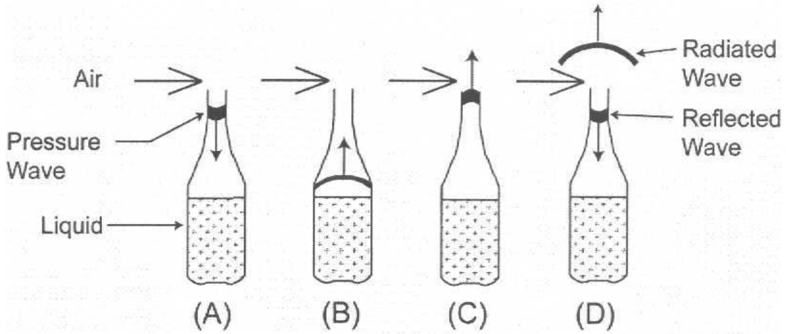
  - The frequency with which the pressure pulses are repeated determines the "pitch" of the sound, with high frequencies producing high pitched sound.

  - The amplitude of the pressure pulses determines the "loudness" of the sound, with large amplitude corresponding to loud sound.

  - The shape of the pressure pulses determines the "tonal quality" of the sound, with smoothly rounded pulses producing a mellow tone and sharp pulses producing a shrill sound.

"POP BOTTLE" WHISTLE

- The whistling sound produced by blowing over the open end of a pop bottle is a good model to introduce the mechanism of pyrotechnic whistles.



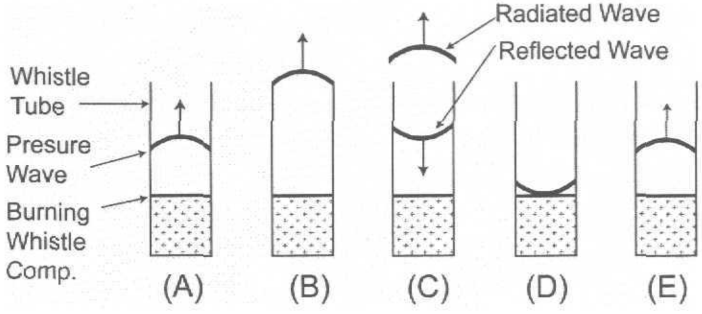
- When air is blown across the top of a pop bottle:

A) A pressure wave passes down into the bottle.
B) It reflects off the liquid surface and returns upward.
C) The pressure wave reaches the mouth of the bottle.
D) Part of the pressure wave passes out of the bottle and part is reflected back into the bottle, strengthened by the air blowing across the mouth. Thus repeating the process over and over again.

- In this way a repeated series of pressure waves are created in the air and are heard as a tone whose pitch (frequency) is determined by the distance from the top of the bottle to the liquid surface.

PYROTECHNIC WHISTLE (SIMPLISTIC)

- **When a pyrotechnic composition, whose burn rate is quite pressure sensitive, burns in a tube, a whistling sound can be produced through a mechanism similar to a pop bottle whistle.**



- **When a whistle composition is burned in a tube:**
  - **A)** A pressure wave rises in the tube.
  - **B)** The pressure wave reaches the end of the tube.
  - **C)** Part of the pressure wave passes out of the tube and part is reflected back into the tube.
  - **D)** When the reflected pressure wave reaches the burning surface, the increased pressure causes the comp. to burn faster.
  - **E)** That produces a pressure wave that rises in the tube, beginning the process over again.

- **In this way a repeated series of pressure waves are created in the air and are heard as a whistle. The pitch is determined by the length of the tube above the present burning surface.**

PYROTECHNIC WHISTLE COMPLEXITIES [DOMANICO]

- **Pyrotechnic whistle compositions seem to burn to produce an intrinsic collection of high frequency sounds. These frequencies are characteristic of the formulation used.**

- **As whistles burn, the output of these high frequencies is roughly constant. However, there is an ever increasing output of low frequency sound.**

- **The net effect of an increasing percentage of lower frequencies is to produce a sound that is perceived to lower in pitch.**

- **The height of the tube above the burning surface still determines the pitch; however, it is more complicated than was previously suggested.**

COMMON WHISTLE FORMULATIONS

- **The most commonly used whistle formulations are:**

Ingredient	Formulation	
Potassium perchlorate	70	70
Sodium salicylate	30	—
Sodium benzoate (a)	—	30

(a) Note that potassium benzoate is also often used.

- **Modifications (Improvements):**
  - Titanium metal (5-15%) can be added to produce white sparks. However, the addition of titanium increases the possibility of accidental ignition during compaction when metal particles may grind against each other.
  - The addition of a few percent paraffin oil aids in compaction, slightly desensitizes the composition, and retards moisture absorption.
  - The addition of a percent or two of iron(III) oxide acts as a catalyst to facilitate the thermal decomposition of the oxidizer.

OTHER WHISTLE FORMULATIONS

- **When the whistle fuel is particularly energetic, potassium nitrate can be used (note formulations 1 & 2).**

Ingredient	1	2	3
Potassium nitrate	50	30	—
Potassium chlorate	—	—	73
Potassium picrate	50	—	—
Potassium dinitrophenate	—	70	—
Gallic acid	—	—	24
Red gum	—	—	3

[All formulations from Ellern].

- **In the past, gallic acid was a commonly used whistle fuel.**
- **The sensitivity to accidental ignition of formulations such as these have made their use uncommon.**

SALUTES OR REPORT SHELLS

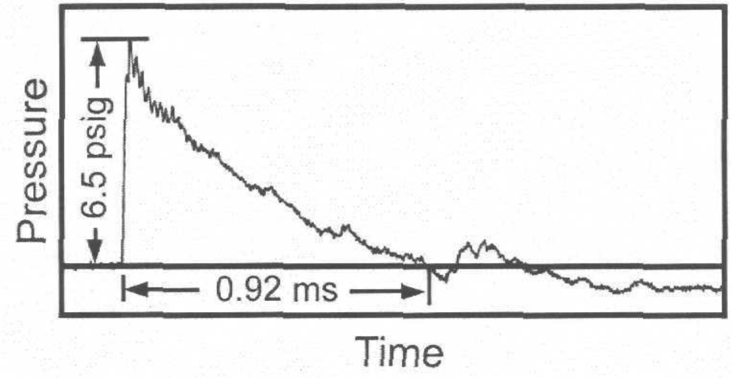
- **Fireworks salutes are explosive devices designed to produce sound by explosion. A salute consists of a paper container, filled with flash powder that has a *means of ignition.***

- **Safety considerations:**
  - **It is essential not to underestimate the power of even small salutes. Work carefully and in as small amounts as practical.**
  - **It is important to avoid the use of chemicals (chlorates and sulfur or sulfides) which add nothing to the level of sound produced, but can greatly increase the sensitivity of flash powder to accidental ignition.** [Shimizu] [Kosanke]:

Ingredient	Formulations	
Potassium chlorate	60	—
Potassium perchlorate	—	70
Aluminum	20	30
Sulfur	20	—
Impact sensitivity height	29 cm	80 cm
Relative loudness	1.0	1.0

BLAST PRESSURE CURVE FOR SALUTE

- **The blast pressure produced by a fireworks salute or military simulator appears as expected for a shock wave.**
  - **Typically the duration of the positive phase will be from about 0.2 to 2 ms.**



- **Curve for 70:30 flash powder (potassium perchlorate:pyro-aluminum) with weak confinement at a distance of 4 feet.**

FLASH POWDER

- All flash powders have been classified as a high explosive by the US BATF.
- Reasonably safe formulations:

Ingredient	Formulation	
Potassium perchlorate	70	—
Barium nitrate	—	68
Aluminum (dark pyro)	30	23
Sulfur	—	9

(Sulfur does not create a sensitivity problem when used with barium nitrate.)

- Burn characteristics of a good flash powder:
  - When unconfined in modest amounts it only burns (i.e., requires strong confinement for explosion).
  - Relatively insensitive to accidental ignition.

THEATRICAL FLASH AND PHOTO FLASH

- For most theatrical and photo flash powders, it is light intensity and not sound levels that are desired.
- Typically this is accomplished by:
  - Using fuel-rich mixtures.
  - Using less powerful oxidizers (like a nitrate rather than potassium perchlorate).
  - Using larger particle sizes, especially for the fuel.
- Typical theatrical and photo flash formulations:

Ingredient	Theatrical	Photo
Potassium nitrate	50	—
Potassium perchlorate	—	30
Barium nitrate	—	30
Magnesium (100 mesh)	50	—
Aluminum (20μ, atomized)	—	40

BULKING AND FLOW AGENTS

- **Flow agents such as magnesium carbonate and fumed silica [Cab-o-sil™ and Sant-o-sil™] are sometimes added to flash powders to facilitate mixing and automated loading.**
- **Fumed silica also helps retard compaction of powders, which can be important for explosive flash powders.**
- **In fireworks, bulking agents such as bran and saw dust are often added to flash powders to help retard compaction.**
- **Some oxidizers are notorious for caking and are now often supplied with anti-cake agents included, for example:**
  - **Potassium chlorate — 0.2% TCP (tri-calcium phosphate)**
  - **Potassium nitrate — 0.1% Petro-AG (sodium dialkylnaphthalene sulfonic acid salt)**

ADDITIONAL FORMULATIONS

Colored Smokes:

	White	Red	Yellow	Green	Blue	Purple
Potassium chlorate	25	30	25	30	30	25
Lactose	25	20	15	20	—	20
Rosin	50	—	—	—	—	—
Methylaminoanthraquinone	—	45	—	—	—	—
Polyvinylacetate	—	5	—	—	—	—
Benzanthrone	—	—	30	—	—	—
Quinoline yellow	—	—	20	15	—	—
Barium carbonate	—	—	10	—	—	—
Solvent green	—	—	—	35	—	—
Indigo	—	—	—	—	40	—
Methylene blue	—	—	—	—	15	—
Starch	—	—	—	—	15	—
Rhodamine B	—	—	—	—	—	55

Comments:

White —*Western Pyrotechnic Association Newsletter*, Vol. 4, No. 3, 1992.
Red, Green and Yellow — "Formulas from the WiZ", *Pyrotechnics Guild International Bulletin*, No. 72, 1990.
Blue — Slight variant of Shimizu's formulation in Lancaster's *Principles and Practice*.
Purple — Source unknown, but it is an excellent formulation.

Whistle Formulations [Conkling]:

	Shrill*	Mellow	Comment:
Potassium perchlorate	70	75	Potassium salt whistles are better starting points for colors other than yellow. Whistle rockets should contain mineral oil or equivalent.
Potassium benzoate	30	—	
Potassium biphthalate	—	25	
Mineral oil	—	+3	

* W.R. Maxwell "Pyrotechnic Whistles".

Magnalium Formulations [Jennings-White]:

Ingredient	Flash Powders		Microstar
Potassium perchlorate	50	—	—
Barium nitrate	—	55	—
Bismuth(III) oxide	—	—	75
Copper(II) oxide	—	—	10
Magnalium (50:50, -60 mesh)	50	—	5
Magnalium (50:50, -200 mesh)	—	35	—
Magnalium (20:80, 200 mesh)	—	10	10

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SECTION 10

APPROACHES TO FORMULATION DEVELOPMENT

- Add a Component
- Substitute a Component
- Mix Compositions
- Triangle Diagrams
- Stoichiometric Approach
- Other Approaches

ADD A COMPONENT

- Simply adding a component to a pre-existing composition can occasionally be used to produce an additional effect or result.

Example: Glitter + Titanium = Flitter Glitter

Ingredient	
Handmade meal powder	50
Barium nitrate	15
Aluminum (atomized, 120-140 mesh)	10
Antimony sulfide	10
Sulfur	5
Dextrin	5
Titanium (10-20 mesh, flake)	5

- This technique is particularly suitable when the material added does not substantially participate in the pyrochemistry.

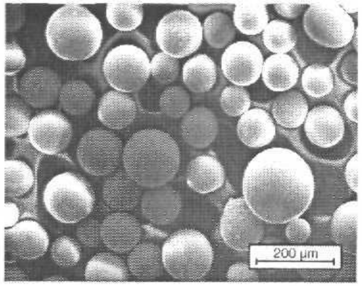
ADD A COMPONENT — TITANIUM

- Coarse to medium grades of titanium are ideally suited for such applications. Generally the titanium only produces additional whitish sparks without seriously disturbing the original pyrochemistry.
- The additional effect of white sparks is produced without altering the primary effect.

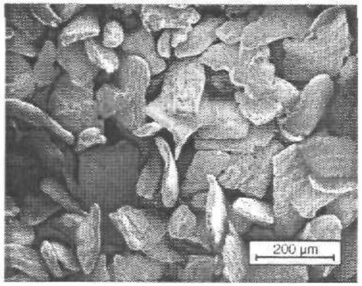
Ingredient	Flash Salute	Whistle	Red Fire	Blue Star	Green Star
Potassium perchlorate	70	70	66	61	16
Barium nitrate	—	—	—	—	42
Aluminum (pyro)	30	—	—	—	—
Magnesium (coated)	—	—	—	—	25
Sodium benzoate	—	30	—	—	—
Accaroid gum	—	—	14	9	—
Parlon	—	—	—	9	—
Polyvinyl chloride	—	—	—	—	15
Strontium carbonate	—	—	20	—	—
Copper carbonate	—	—	—	12	—
Rice starch (glutinous)	—	—	—	5	—
Titanium	+15	+15	+15	+10	+20

TITANIUM PARTICLES

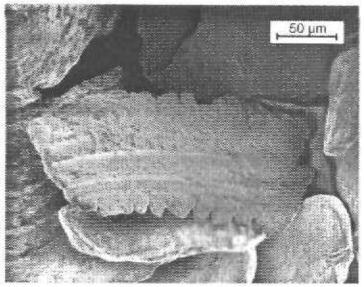
- Top, spherical atomized
- Middle, chipped flakes (note tool marks)
- Bottom, sponge (note porous nature)



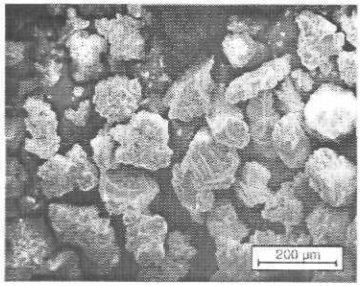
Atomized Spherical



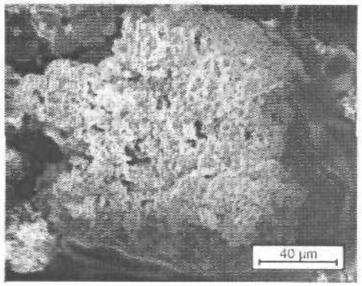
Pyro Flake



Close up



Sponge



Close up

ADD A COMPONENT — ADDITIVES

- The addition of materials in small or very small amounts often will not significantly deteriorate the primary effect, but can accomplish important secondary effects.
  - Examples:

Burn catalyst — 2% Fe_3O_4
(Aids the decomposition of $KClO_4$.)

Acid neutralization — 1% $BaCO_3$
($2\ H^+ + CO_3^- \rightarrow CO_2 + H_2O$)

Aluminum pacification — 0.5% Boric acid
(Strengthens protective oxide coating.)

Propagation improvement — 0.2% Lampblack
(Dark color absorbs radiant flame energy.)

Static control — 0.1% Conductive lampblack
(Conducts electrostatic charges from sulfur to make it free flowing.)

Anti-caking — 0.05% Petro-AG in KNO_3
(Sodium dialkylnaphthalene sulfonic acid salt.)

ADD A COMPONENT — FAILURES

- In some cases the addition of a new component does not destroy the original effect, but proves to be completely (or mostly) ineffective in producing the additional effect desired.
  - For example adding a chlorine donor to barium nitrate flash powder to produce a green flash.
    - At the temperatures produced by burning flash powder, the green color species (BaCl and BaOH) are destroyed. Also, the incredibly bright, incandescent Al_2O_3 particles completely overwhelm any slight production of green light.
- In some cases, the addition of a new component completely destroys the original effect.
  - For example, the addition of a chlorine donor to produce green glitter, using the previous $Ba(NO_3)_2$ based formation, completely destroys the glitter chemistry.

SUBSTITUTE A COMPONENT

- Substituting for all or part of a component in a preexisting composition often can be used to modify or improve a formulation.

  - Example: Convert a red formulation to purple by substituting copper(II) oxide for half the strontium carbonate.

Ingredient	Red No. 4 [Bases]	Purple [Bases/Baechle]
Potassium perchlorate	35	35
Ammonium perchlorate	30	30
Hexamine	10	10
Accroides resin	5	5
Strontium carbonate	20	10
Copper(II) oxide	—	10

Note 1: These formulations are for lances, not stars.

Note 2: If necessary, slightly more oxidizer can be used to help burn away the lance tubes.

  - When an ingredient in a favorite formulation becomes expensive or is no longer available, often substitution is the easy alternative to complete reformulation.

MIX COMPOSITIONS

- When two pre-existing compositions are chemically compatible, often useful new effects can be produced by simply mixing them in various proportions.

- CAUTION: When using this approach, serious consideration must be given to the possibility that dangerous chemical combinations might be created by such mixing. (Discussed in "Pyrotechnic Sensitivity," Module.)

- This technique is very useful for easily producing composite colors and is the basis of Baechle and Veline's Color Mixing System.

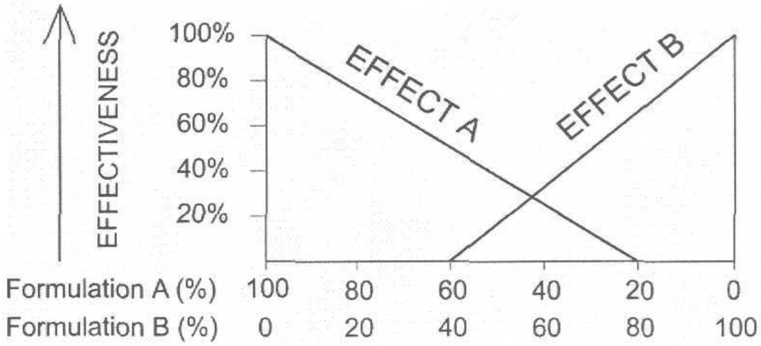
  - A set of four high quality color star formulations were developed – Red – Orange – Green – Blue.

  - These formulations are fully compatible with one another, such that mixtures of the formulations do not interfere with each other's color production.

REQUIREMENT FOR SUCCESSFUL MIXING TO PRODUCE COMBINED EFFECTS

- When two pre-existing compositions are combined in various proportions, useful results are not guaranteed.

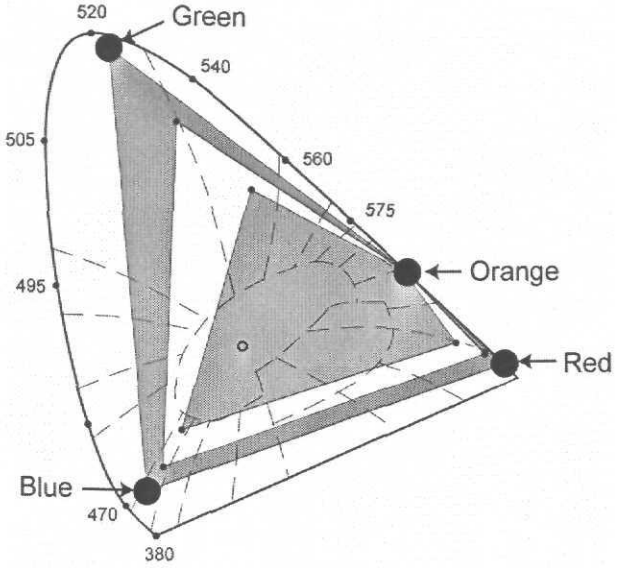
- As the second formulation is added, there will generally be a reduction in the effectiveness of the first formulation.



- Hopefully, as more of the second formulation is added, before the effectiveness of the first is reduced to zero, a useful amount of the new effect will be produced.

STAR COLOR MIXING SYSTEM [VELINE]

- Using the four primary mixes, many interesting colors can easily be made. (Note that the assignment of the color points are only guesses for illustration.)



- Using binary mixes, all of the colors along the lines connecting the primary colors can be made.

- Using ternary or quaternary mixes, all of the colors inside the lines can be made.

A COMPATIBLE STAR FORMULA SYSTEM FOR COLOR MIXING [VELINE]

- **Basic (Compatible) Color Star Formulations:**

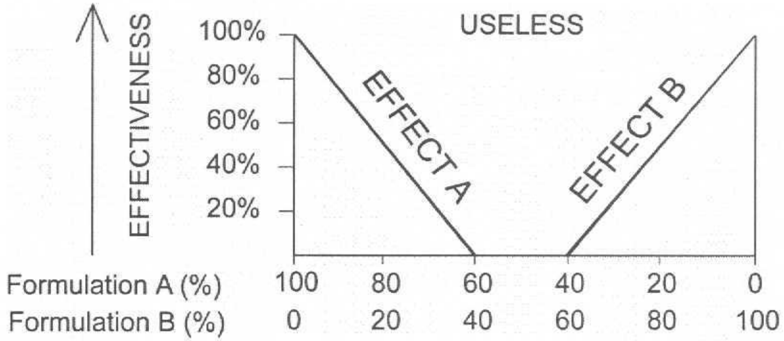
Ingredient	RED	ORANGE	GREEN	BLUE
Potassium perchlorate	55	55	30	55
Barium nitrate	—	—	24	—
Strontium carbonate	15	—	—	—
Calcium carbonate	—	15	—	—
Barium carbonate	—	—	15	—
Copper(II) oxide	—	—	—	15
Parlon	15	15	15	15
Red gum	9	9	5	9
Magnalium (50/50) -200	6	6	11	6
Dextrin	+4	+4	+4	+4

- **Mixing to produce composite colors:**

	Parts by weight of above formulations			
New Color:	RED	ORANGE	GREEN	BLUE
Yellow	—	45	55	—
Chartreuse	—	20	80	—
Aqua	—	—	80	20
Turquoise	—	—	55	45
Magenta	50	—	—	50
Maroon	85	—	—	15
Peach	25	60	—	15
Purple	15	5	—	80

UNSUCCESSFUL MIXING TO PRODUCE COMBINED EFFECTS

- **As the second formulation is added, it is more likely that the first effect will be totally destroyed before a useful new effect is produced.**



- **This is often the case, and must result from some form of functional incompatibility between the two formulations.**

RESULTS OF BLUE WHISTLE EXPERIMENTS

- The following experiments attempt to make a blue whistle by mixing a whistle formulation (A) and a similar blue formulation (B).

Formulation A:
70 Potassium perchlorate + 30 Potassium benzoate
Formulation B:
82 Ammonium perchlorate + 18 Copper(II) benzoate

Formulation A (Whistle)	Formulation B (Blue)	Effect A (Whistle)	Effect B (Blue)
100	0	+	O
90	10	+	O
80	20	O	O
70	30	O	O
60	40	O	+
50	50	O	+

Note: O ≡ No effect produced.
+ ≡ Successful effect resulted.

- The intermediate compositions produce neither whistle nor blue. Therefore, in this case, the approach (mixing compositions) is not useful.

UNDERSTANDING TRIANGLE DIAGRAMS

- Triangle diagrams can aid in development of complex formulations and in visualization of results.

- First, in complexity, is developing a two component composition, such as a blue made using ammonium perchlorate + copper(II) benzoate [Bleser].
  - Here the question is: What proportion of the two materials should be used?
  - It is fairly trivial; however, it may be useful to display the results using a "Line Diagram".

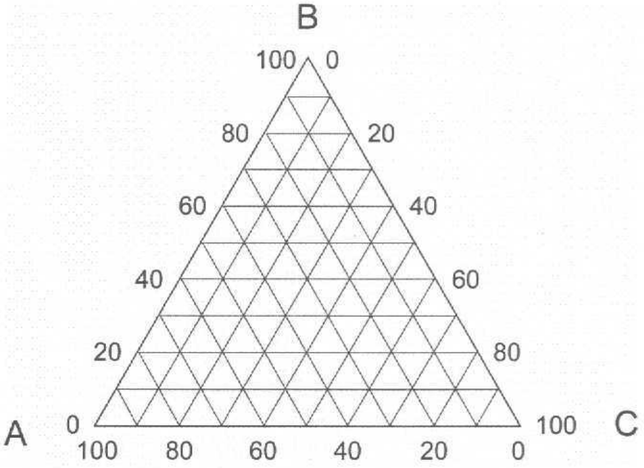
Ammon. perchl.	100	80	60	40	20	0
Cu(II) benzoate	0	20	40	60	80	100

= Each possible formulation is represented by a point somewhere along this line.

- Note: There is no one optimum formulation. It could be optimized for burning speed, for brightness, or for color purity.

UNDERSTANDING TRIANGLE DIAGRAMS (Continued)

- **Next in complexity are three component pyrotechnic systems. They require a triangle diagram for graphic representation.**

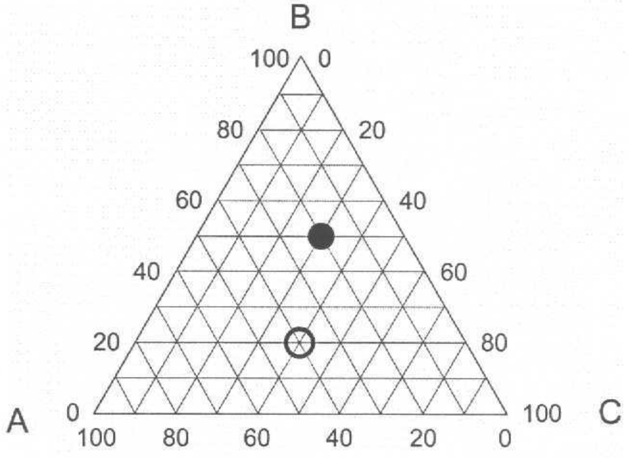


- **Each side of the triangle is used to record the percentage of one of the components. The amount of that component ranges from 0% to 100%. (Similar to the 2-component case above.)**

- **The vertices (points) of the triangle diagram correspond to 100% of one component and 0% of the other two. As a convention, each vertex is labeled for the component for which it represents 100%.**

UNDERSTANDING TRIANGLE DIAGRAMS (Continued)

- **Each point inside the triangle diagram represents a specific trio of percentages of components, always adding to 100%.**



- **For example points "O" and " ● " correspond to the following compositions:**

O = 40% A, 20% B, 40% C.

● = 20% A, 50% B, 30% C.

- **Triangle diagrams are difficult to comprehend when first experienced.** [For more help, see Kosanke, 1982.]

TRIANGLE DIAGRAM
GUIDING FORMULATION DEVELOPMENT

- Consider the following set of results:

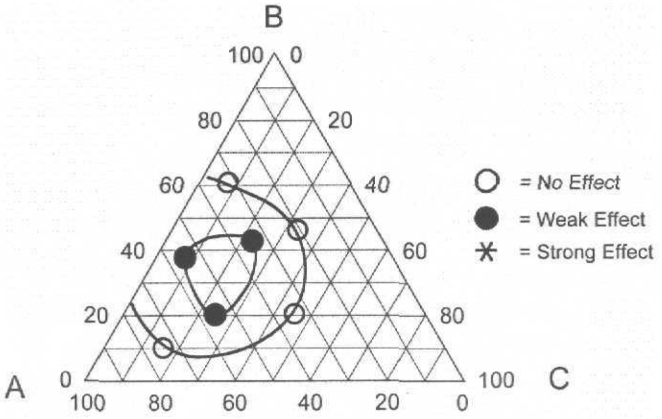
Trial No.	% A	% B	% C	% D	Result
1	34	21	45	+5	No effect
2	56	20	24	+5	Weak effect
3	75	10	15	+5	No effect
4	33	43	24	+5	Weak effect
5	20	47	33	+5	No effect
6	55	38	7	+5	Weak effect
7	32	62	6	+5	No effect
Final	?	?	?	?	Strong effect

- Examining these data, it is not obvious what formulation should be tried next.

TRIANGLE DIAGRAM GUIDING FORMULATION DEVELOPMENT (Continued)

- Often, by recording the results of test formulations on a triangle diagram, rapid progress toward the best formulation will be facilitated.

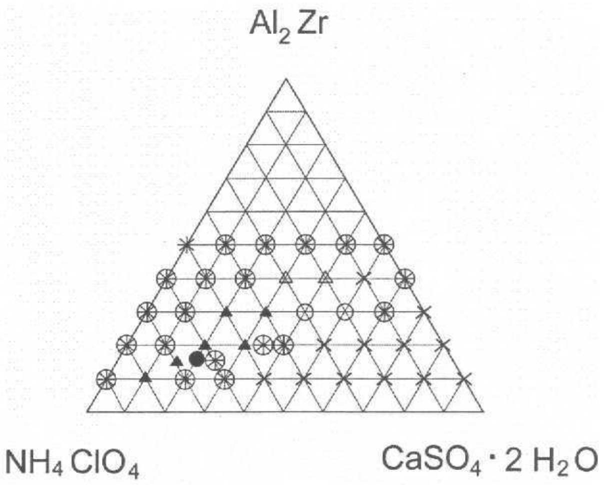
- By presenting these data as a triangle diagram, it is relatively easy to choose a formulation with a high probability of success.



  - *Roughly add lines, as on a contour map, to form a crude "Bull's Eye" (target).*
  - You would expect to find the best effect produced somewhere near the center of the target.

TRIANGLE DIAGRAM — PRESENTING COMPLEX AND VARIED RESULTS

- **The results from many trials can be clearly presented on a single triangle diagram.**
- **For example:**



Symbols	Description
●	Good color, blinks sharply.
○	Not good color, but blinks sharply
▲	Good color, sometimes blinks and sometimes burns continuously
△	Not good color, sometimes blinks and sometimes burns continuously
✖	Does not ignite or burn
⊛	Continuous burning with a bright flame
✳	Continuous burning followed by "detonation".

TRIANGLE DIAGRAMS FOR MORE THAN THREE COMPONENT SYSTEMS

- **The vertices of triangle diagrams may be:**
  - **Single components.**
  - **Binary mixtures.**
  - **Ternary mixtures (for example, results from another triangle diagram).**
  - **Complex mixtures (for example, determined stoichiometrically).**
  - **Finished compositions.**
  - **Any combination of the above.**
- **Some components can be considered "fixed" in the composition and not included in the triangle diagram. For example:**
  - **Binder = 5% or**
  - **Color agent = 15%**

STOICHIOMETRIC APPROACH

- Formulations can be developed by the quantitative use of chemical equations.
- For example, consider the development of an Iodine-based Smoke Composition.
  - — **Step 1** Determine materials to be used. In this case, calcium iodate and magnesium.
  - — **Step 2** Decide what the most likely reaction products are. In this case, calcium oxide, magnesium oxide and iodine.
  - — **Step 3** Write the balanced chemical equation(s):

$$Ca(IO_3)_2 + 5\ Mg \rightarrow CaO + I_2 + 5\ MgO$$

  - — **Step 4** Look up or calculate the required molecular weights [$Ca(IO_3)_2$].

1 x Ca = 1 x 40 = 40
2 x I = 2 x 127 = 254
6 x O = 6 x 16 = 96
Total 390

STOICHIOMETRIC APPROACH (Continued)

- — **Step 5** Calculate the required weights for stoichiometric reaction.

Formula	Moles Req.		Mol. Wt.	Weight Req. (g)	Percentage
$Ca(IO_3)_2$	1	x	390	390 ÷ 510	76.5%
Mg	5	x	24	120 ÷ 510	23.5%
				510	

- — **Step 6** Adjust formulation as desired or needed.

- In this case, to avoid reaction between magnesium and the iodine produced, we could cut back the magnesium content, for example:

Calcium Iodate	80%
Magnesium* (–50 mesh)	20%

* coated with linseed oil

STOICHIOMETRIC DEVELOPMENT OF A GLITTER FORMULATION

- Suppose a long delay glitter formulation is desired. All the potassium should end up as the disulfide or the thioantimonate as the spritzel leaves the star. Let us choose these two products to be half and half, and set up the appropriate equations:
  - Formation of potassium disulfide:

$$2\ KNO_3 + 3\ C + 2\ S \rightarrow K_2S_2 + 3\ CO_2 + N_2$$

  - Formation of potassium thioantimonate:

$$2\ KNO_3 + 3\ C + S \rightarrow K_2S + 3\ CO_2 + N_2$$

$$K_2S + 1/3\ Sb_2S_3 \rightarrow 2/3\ K_3SbS_3$$

- By adding these equations:

$$4\ KNO_3 + 6\ C + 3\ S + 1/3\ Sb_2S_3 \rightarrow 2/3\ K_3SbS_3 + K_2S_2 + 6\ CO_2 + 2\ N_2$$

STOICHIOMETRIC DEVELOPMENT OF A GLITTER FORMULATION (Continued)

- Remember, it is possible to increase the delay and brighten the flash by replacing some of the potassium nitrate with an equivalent amount of barium nitrate.
  - Thus, instead of 4 KNO_3, use 3 KNO_3 and 1/2 $Ba(NO_3)_2$
- The balanced equations give the number of moles of each material required for stoichiometric reaction. Multiplying by the respective molecular (or atomic) weights gives the required weight of each material, as below.

Component	Moles Req.		Molecular Weight		Weight Required (grams)
KNO_3	3	×	101	=	303
$Ba(NO_3)_2$	1/2	×	261	=	131
C	6	×	12	=	72
S	3	×	32	=	96
Sb_2S_3	1/3	×	340	=	113

STOICHIOMETRIC DEVELOPMENT OF A GLITTER FORMULATION (Continued)

- Because charcoal is used instead of pure carbon, and the carbon content of charcoal is about 90%, the required weight of charcoal is 72 ÷ 0.9 = 80 grams.

- *Therefore the total weight of materials would be:*

  303 + 131 + 80 + 96 + 113 = 723 grams

- It will simplify matters by arbitrarily fixing the content of binder and metal. It is known that 5% dextrin and 10% aluminum are typical. Thus the stoichiometrically determined materials will constitute 85% of the final composition.

- Accordingly, to find the formulation it is necessary to multiply the weights by 85/723.

STOICHIOMETRIC DEVELOPMENT OF A GLITTER FORMULATION (Continued)

- This gives the following theoretical formulation.

	Theoretical	Oglesby
Potassium nitrate	36	35
Barium nitrate	15	16
Charcoal	9	9
Sulfur	11	11
Antimony sulfide	13	13
Aluminum	10	10
Dextrin	5	5

  - Note that proportions have been rounded to the nearest percent.

- The theoretical formulation is very nearly the long delay glitter given by Oglesby.

FORMULATION DEVELOPMENT BY OBSERVATION, LOGIC, INTUITION AND SERENDIPITY

- Strobe example — Serendipity:
  - Ellern Formula 46 for gun simulator = 1 / 1 / 1 $KClO_4$ / Mg:Al / Navy SPD propellant powder.
  - Not having Navy SPD propellant, try using guanidine nitrate instead. (It is a gas producer that is a fuel–oxidizer combination.)
  - Burning results in strobe.
- Strobe example — Observation:
  - Sam Bases notes that his ammonium perchlorate red star formulation with the highest hexamine content (15%) is bright, with excellent color, but has a tendency to go out.
  - Note: Composition going out = 1/2 of a strobe cycle.

FORMULATION DEVELOPMENT BY OBSERVATION, LOGIC, INTUITION AND SERENDIPITY (Continued)

- Observation:
  - Red star formulation:

Ingredient	Formulation
Strontium nitrate	40
Ammonium perchlorate	35
Hexamine	20
Polyvinyl acetate	5

  - Exhibits unstable burning properties.
  - Note: Unstable burning implies incipient strobe.
- Serendipity — but should possibly have been logic.
  - Trying to make lithium red color.
  - Better lithium colors result from a cool flame, and hexamine is a cool fuel; use lots of it.

Lithium perchlorate	1
Hexamine	1

  - It Strobes! But this should not have been a great surprise because of two prior observations.

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SECTION 11

PYROTECHNIC SENSITIVENESS

- Water Reactivity
- Auto-Ignition Temperature
- Friction Sensitiveness
- Impact Sensitiveness
- Electrostatic Sensitiveness
- Cautions about Sensitiveness Indicators

SENSITIVENESS AND SENSITIVITY

- Definitions from the UK Sensitiveness Collaboration Committee:
  - Sensitiveness: A measure of the relative probability of an explosive being ignited or initiated by a prescribed stimulus.
  - Sensitivity: A measure of the stimulus required to cause reliable design-mode functioning of an explosive system.
- In the US, sensitivity has been the term used regarding both probability and stimulus level.
- For the purpose of these notes:
  - Sensitiveness is the probability of ignition from a specified level of stimulus. For example, the sensitiveness of some test composition to an electrostatic discharge of 3.5 J might be 0.25.
  - Sensitivity is the stimulus level (energy) required to cause an ignition in a specified fraction of trials. For example, the 50% sensitivity of some test composition to impact might be expressed as 30 cm (for one type of instrument).

PYROTECHNIC SENSITIVENESS

- Because incendiary and explosive output of pyrotechnic materials can be equally devastating, rating their hazard can amount to rating their potential for accidental ignition.
- Sensitivity to accidental ignition can be characterized in 5 areas:
  - Water reactivity.
  - Auto-ignition temperature.
  - Impact sensitiveness.
  - Friction sensitiveness.
  - Electrostatic sensitiveness.
- Often there is little relationship between the above 5 indicators. Thus something must be known of each of these to assess the relative danger of a pyrotechnic composition.

PYROTECHNIC SENSITIVENESS (Continued)

- You should know something about the sensitiveness of all the pyrotechnic compositions used. This can come from:
  - Information from others:
    - = Firm technical data (good).
    - = Anecdotal stories (better than nothing).
  - General personal knowledge of sensitiveness characteristics of chemicals and combinations (OK).
  - Actual testing of compositions (best).
- Relatively good and reliable sensitiveness screening data can be collected, using simple and very inexpensive equipment.
  - The design and use of this simple equipment will be illustrated in this section.

WATER REACTIVITY

- Water reactivity is an expression of the likelihood of occurrence of exothermic or other undesirable chemical reactions upon the addition of water to a pyrotechnic composition. In some cases these reactions can lead to ignition.
- Some of the compositions to be suspicious of are those containing:
  - Magnesium (for example with silver nitrate)
  - Magnalium
  - Aluminum (for example with iodine)
  - Zinc (for example with ammonium nitrate)
- Ignition will occur for the above combinations, even when present in very small amounts, when they are dampened with water.
- New (unfamiliar) compositions containing these metals should be tested in small quantity, for water sensitivity, before larger amounts are dampened or put away for drying. Testing often consists of observing for a temperature rise over time (with or without instruments).

WATER REACTIVITY (Continued)

- In addition to heat production, gas production or an odor upon wetting can be an indication that undesirable chemical reactions are occurring.
  - For example, production of hydrogen gas (odorless) or ammonia gas.

$$Mg + 2\,H_2O \rightarrow H_{2(g)} + Mg(OH)_2$$

$$6\,KNO_3 + 16\,Al + 9\,H_2O \rightarrow 6\,KAlO_2 + 5\,Al_2O_3 + 6\,NH_{3(g)}$$

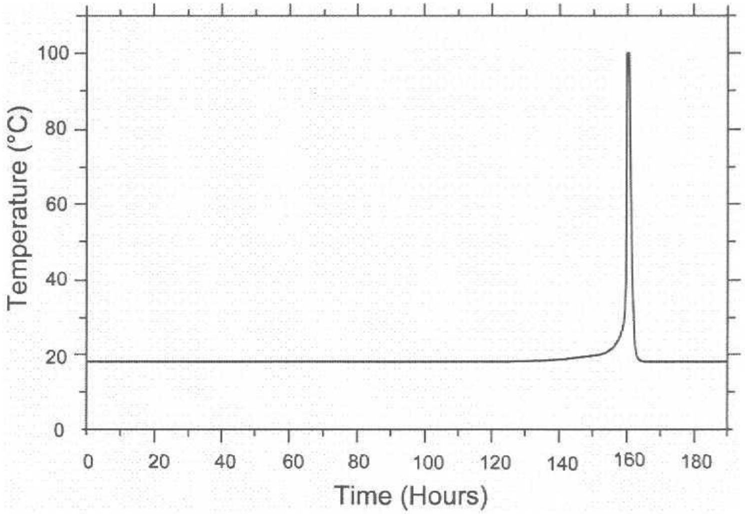
- Water reactivity also includes chemical reactions that do not produce heat, but rather produce new (undesirable) chemicals.
  - For example, double decomposition (“metathesis”) to produce ammonium chlorate (spontaneously explosive) or ammonium nitrate (hygroscopic).

$$NH_4ClO_4 + KClO_3 \rightarrow NH_4ClO_3 + KClO_4$$

$$NH_4ClO_4 + KNO_3 \rightarrow NH_4NO_3 + KClO_4$$

ALUMINUM / WATER REACTIVITY

- Although it is often felt that aluminum is not water reactive, this is not true. (Alcan S-10, 12 μ, spherical, atomized aluminum plus distilled water at 18 °C).

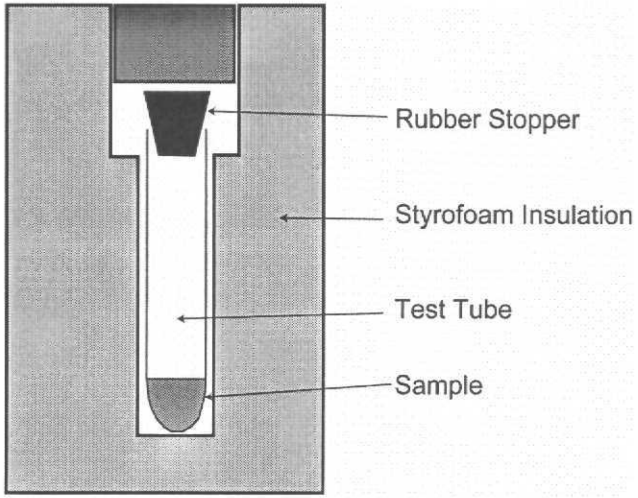


- Note that there was a prolonged delay (almost 7 days) before the manifestation of the reaction and that there was essentially no warming before the thermal peak.

- At higher temperatures or under alkaline (basic) conditions, this water reaction will be almost instantaneous.

WATER REACTIVITY SCREENING APPARATUS

- Simple screening apparatus



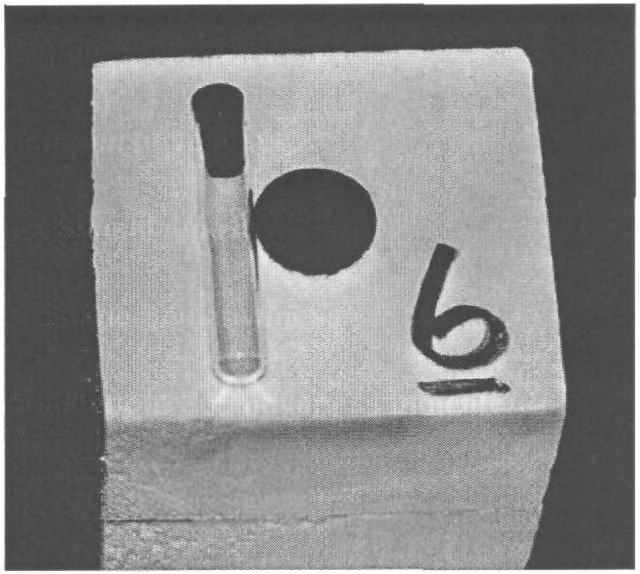
- The sample is 4 to 6 grams of a 50:50 mixture of the test composition and water.

- After several days, observe to determine whether the stopper has loosened, the sample has dried, or an odor has been produced. If so, there has been a reaction with the water.

    - However, note that double decomposition reactions can occur without the above indications.

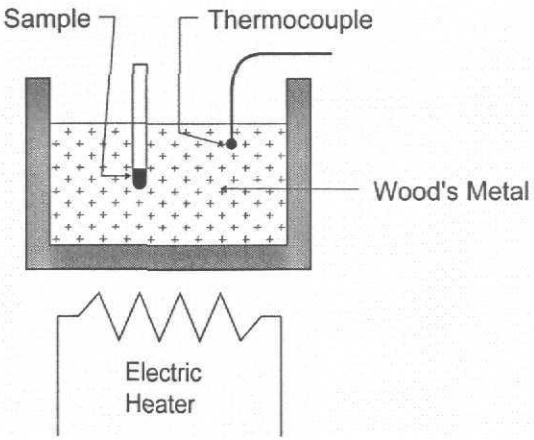
WATER SENSITIVITY SCREENING APPARATUS
(Continued)

- Example of a very simple and very inexpensive water sensitivity screening apparatus.



AUTO-IGNITION TEMPERATURE

- Auto ignition temperature is the temperature to which a small sample of pyrotechnic composition must be heated to cause it to spontaneously ignite.
- There are several methods of auto-ignition temperature measurement. One type uses a sample placed in a heated bath of Wood's metal.



- Bath temperature is raised at a rate of 5 °C per minute and the bath temperature when the sample ignites is reported as the ignition temperature.

AUTO-IGNITION TEMPERATURE (Continued)

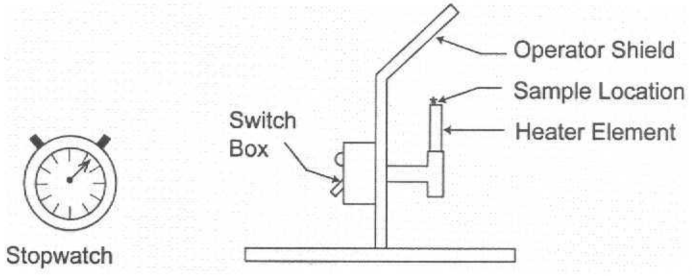
- **Ignition temperatures for mixtures of magnesium and various oxidizers, and for potassium chlorate and various fuels** [Shidlovskiy]:

Mg + Oxidizer	Ignition Temp. °C	$KClO_3$ + Fuel	Ignition Temp. °C
$KClO_3$	540	Lactose	195
$Sr(NO_3)_2$	610	Sulfur	220
$Ba(NO_3)_2$	615	Shellac	250
$NaNO_3$	635	Charcoal	335
KNO_3	650	Magnesium	540
$KClO_4$	715	Aluminum	785

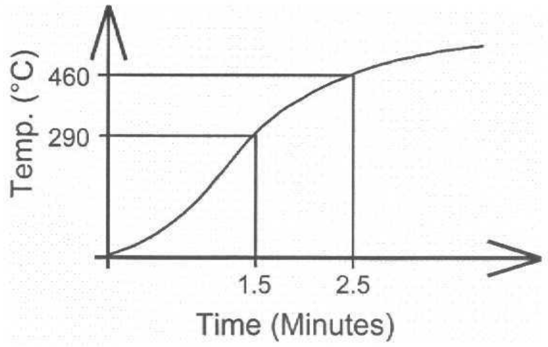
- **Chemical combinations to be suspicious of:**
  - **Those containing a chlorate.**
  - **Those containing low melting point fuels.**
  - **Especially those containing both of above.**
- **Because of differences in test methods, it is not unusual to find a range of ignition temperatures reported for the same pyrotechnic material.**

IGNITION TEMPERATURE SCREENING APPARATUS

- **Simple screening test apparatus:**

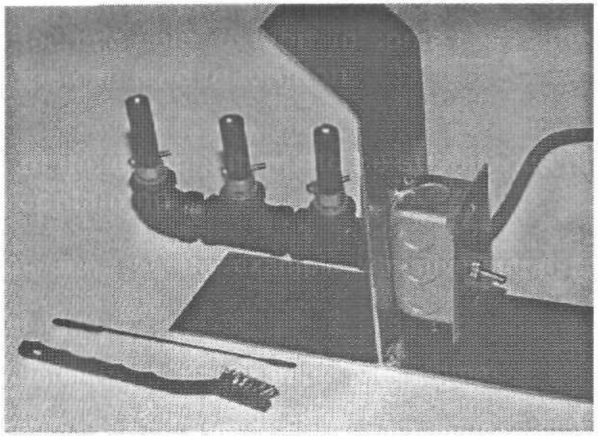


- **Prepare a graph of temperature as a function of time after heater is turned on. (A thermocouple gauge can be used to measure temperatures.)**

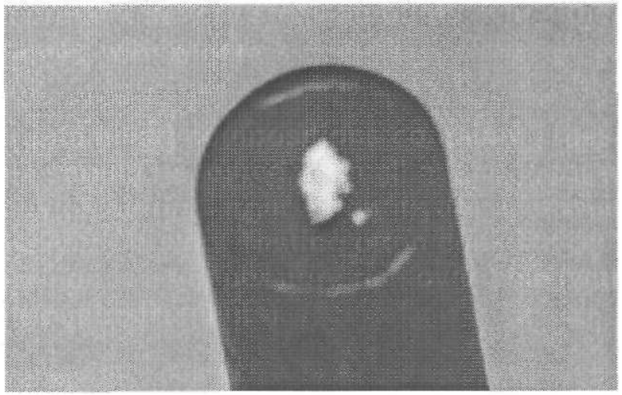


IGNITION TEMPERATURE SCREENING APPARATUS
(Continued)

- Example of a very simple and very inexpensive auto-ignition temperature screening apparatus.



- Test sample in place on heating element.



IGNITION TEMPERATURE SCREENING

- When performing these tests, observation of sample decomposition before ignition may indicate suspect results. In larger quantities, such a sample may ignite at about the temperature where decomposition was observed.

- Suggested sensitivity ranges for one type of heating element.

Time to Ignition (min.)	Approximate Temperature (°C)	Thermal Sensitivity
< 1.5	< 290	Very sensitive
1.5 – 2.5	290 – 460	Sensitive
> 2.5	> 460	Relatively insensitive

- Note that the choice of the various sensitivity ranges was somewhat arbitrary. These should be adjusted as appropriate for different situations.

FLASH POWDER THERMAL SENSITIVITY

- Test of common fireworks flash powders:

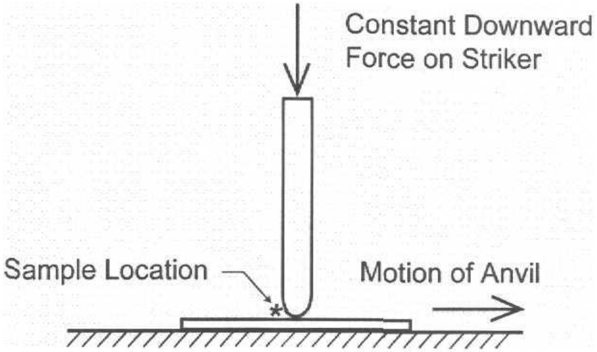
Ingredient	I	II	III
Potassium chlorate	5	—	—
Potassium perchlorate	—	4	7
Antimony sulfide	1	1	—
Aluminum (German dark)	1	1	3

- Auto ignition temperatures:

Flash Powder	Time to Ignition	Auto. Ign. Temp. °C	Sensitivity
I	≈1:25	≈260	Very sensitive
II	≈2:20	≈435	Sensitive
III	>4:00	>570	Relatively insensitive

FRICTION SENSITIVITY

- Friction sensitivity is a measure of a material's tendency to ignite in response to energy input as friction. Often a sample is placed between two surfaces (one rounded and one flat), which are pressed together. In the test, the two surfaces are moved relative to each other.

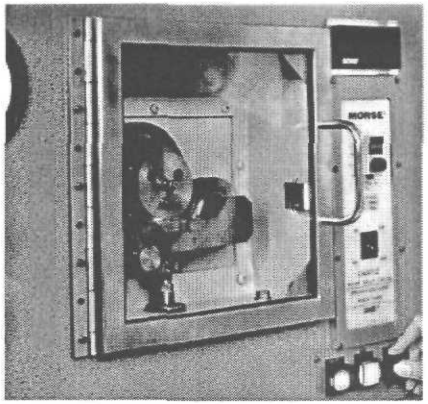


- Friction sensitivity is often reported as the force applied to the striker that is sufficient to initiate a reaction (in a specific percentage of trials). However, because of differences in test methods, it is not unusual to find a range of values reported for the same pyrotechnic material.

- Lubricants in pyrotechnic formulations tend to reduce friction sensitivity, while hard gritty materials tend to increase friction sensitivity.

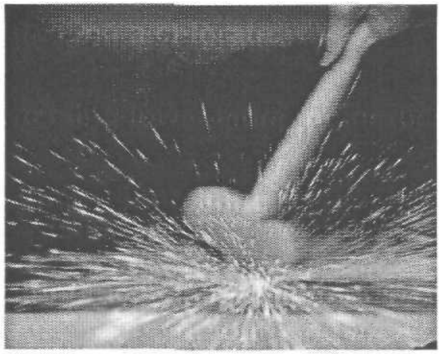
EXAMPLES OF FRICTION SENSITIVENESS TESTERS

- **Rotary friction tester apparatus.**



(Photo courtesy of UK Health and Safety Laboratory)

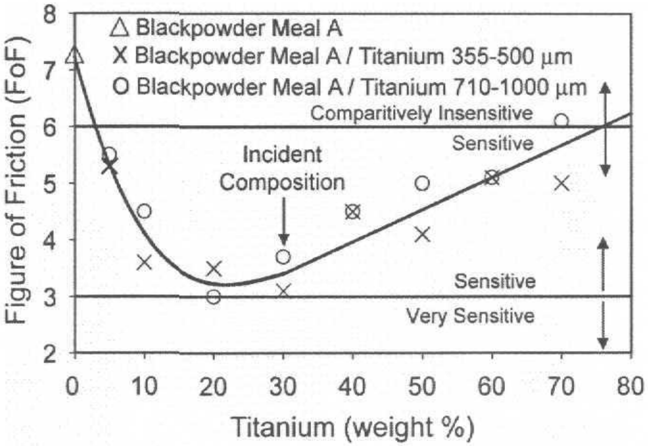
- **Mallet friction test in progress.**



(Photo courtesy of UK Health and Safety Laboratory)

GERB / FOUNTAIN LOADING ACCIDENTS

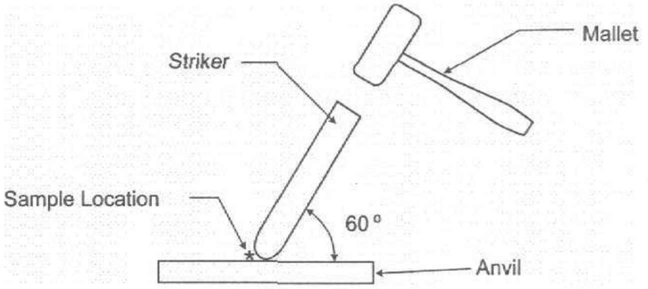
- **Mixtures of Black Powder with titanium, used to produce fountains with white sparks, have not been considered to be particularly dangerous. However, two recent accidents (one fatal) while loading gerbs have caused these mixes to be examined closer.**
- **Friction sensitivity of Black Powder / titanium sponge mixes** [Wharton]**:**



- **Note that maximum friction sensitivity occurs when Ti ranges from 20 to 30% and is mostly independent of Ti particle size in the range from ≈15 to ≈45 mesh.**

FRICTION SENSITIVENESS SCREENING APPARATUS

- Simple screening test apparatus:



Striker materials — Hardwood (dowel)
— Steel (rod)

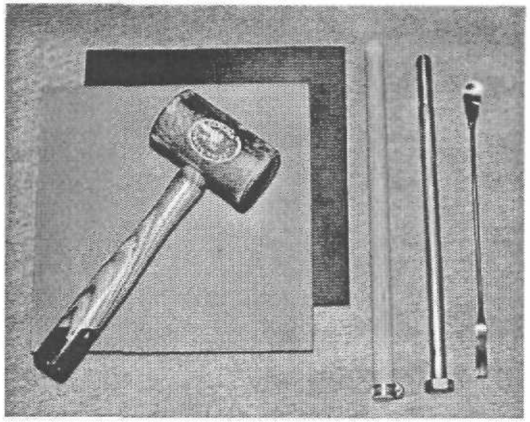
Anvil materials — Hardwood
— Steel plate

Note: This test includes a component of impact as well as friction sensitivity testing.

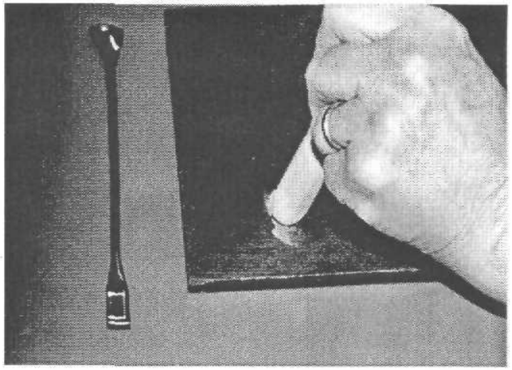
- This test is similar to the old US BOM "Broom Stick" test (ca. 1930) and the "Mallet" test recently developed for use in the UK.
- In these tests any of the following is an indication of an ignition: sparks, flash, snap, or smell of reaction products.

FRICTION SENSITIVENESS SCREENING APPARATUS (Continued)

- Example of very simple and very inexpensive friction sensitiveness screening apparatus



- Friction sensitiveness test in progress.



FRICTION SENSITIVITY SCREENING APPARATUS
(Continued)

- Sensitivity ranges for simple screening test apparatus:

Result:

Y ≡ 1 or more ignitions in 5 trials.

N ≡ <1 reaction in 5 trials.

- If there is only one ignition in 5 trials, perform at least a second set of 5 trials to be more certain whether the test should be scored Y or N.

Striker	Anvil	Result	Friction Sensitivity
Wood	Wood	Y	Very sensitive
Wood	Steel	Y	Sensitive
Steel	Steel	Y	Mildly sensitive
Steel	Steel	N	Relatively insensitive

- Note that the choice of striker and anvil materials and the sensitivity ranges were somewhat arbitrary. These should be adjusted for specific needs.

FLASH POWDER FRICTION SENSITIVITY

- Common flash powders:

Ingredient	I	II	III
Potassium chlorate	5	—	—
Potassium perchlorate	—	4	7
Antimony sulfide	1	1	—
Aluminum (German dark)	1	1	3

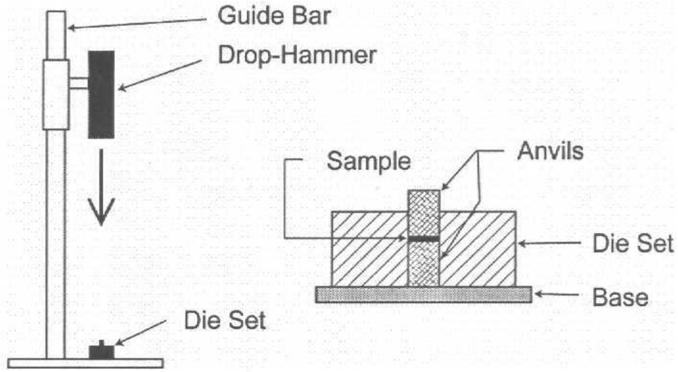
- Friction sensitivity:

Flash Powder	Highest “Yes” (Striker / Anvil)	Friction Sensitivity
I	Wood / Wood	Very sensitive
II	Wood / Steel	Sensitive
III	Steel / Steel	Mildly sensitive

- Sound levels of salutes made with these three formulations are all about the same.

IMPACT SENSITIVITY

- **Impact sensitivity is a measure of a material's tendency to ignite in response to energy input as an impact.**

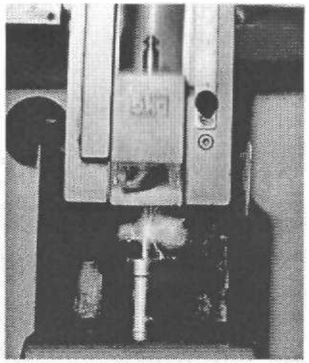


- **A sample is placed between two steel anvils. A drop-hammer is allowed to fall on the upper anvil, which transfers the impact to the sample.**

- **Impact sensitivity is reported as the height of drop-hammer that results in ignition (in some specific percentage of the trials). Generally, 2 kg and 5 kg drop-hammers are used. Often the surface of the anvil in contact with the sample is about 0.5 cm^2. Because of differences in test methods, it is not unusual to find a range of values reported for the same pyrotechnic material.**

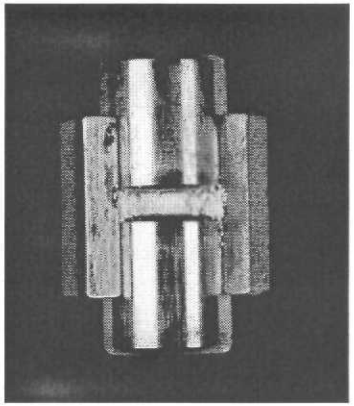
EXAMPLE OF IMPACT SENSITIVENESS TESTER

- **Five kg Drop Hammer Apparatus.**



(Photo courtesy of UK Health and Safety Laboratory)

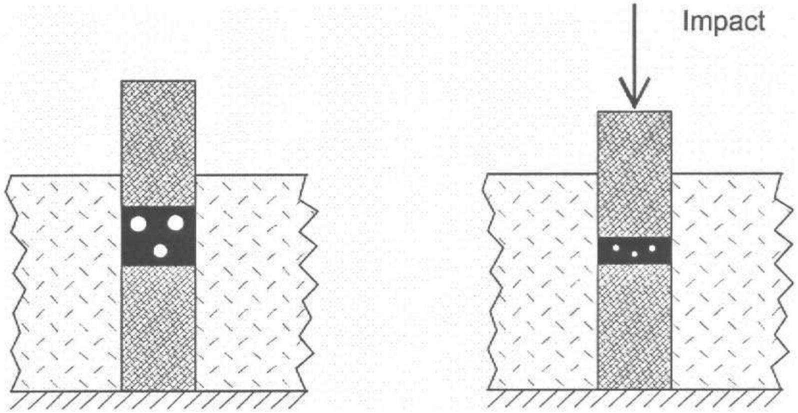
- **Impact die set and sample.**



(Photo courtesy of UK Health and Safety Laboratory)

IMPACT SENSITIVITY (Continued)

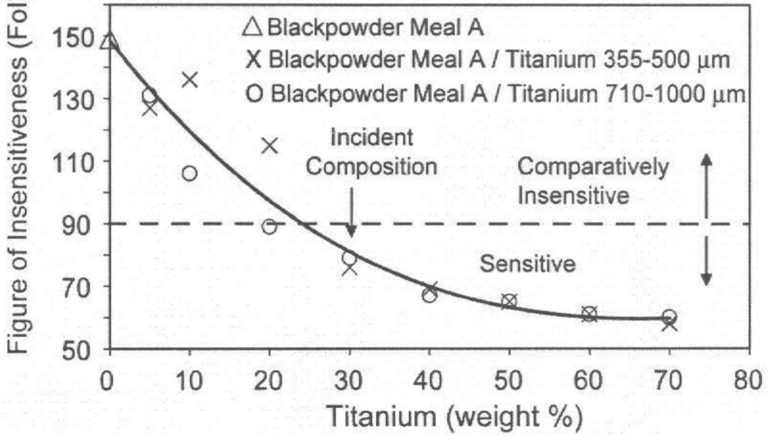
- **When a sample is subjected to an impact, there is an element of friction included, as grains of composition rub against each other as the sample is rapidly compressed. However, entrapped gases also undergo compressive heating, which results in "hot spots."**



- **If the temperature of the hot spots is sufficiently high, combined with thermal friction effects, it is possible that the impacted sample will ignite.**

BLACK POWDER / TITANIUM IMPACT SENSITIVITY

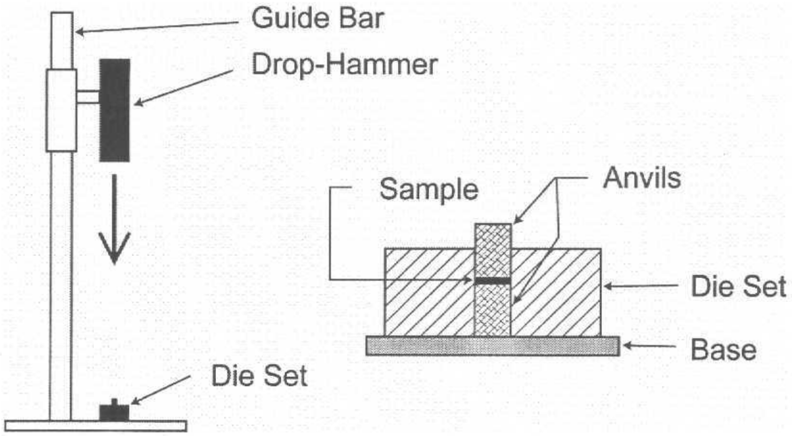
- **In further examinations of the Black Powder and titanium sponge mixtures, which resulted in manufacturing accidents, their impact sensitivities were determined** [Wharton].



- **Note that impact sensitivity increases continuously with increasing Ti percentage, unlike friction sensitivity discussed earlier. Again note that sensitivity is mostly independent of Ti particle size in the range from ≈15 to ≈45 mesh.**

IMPACT SENSITIVENESS SCREENING APPARATUS

- Simple screening test apparatus:



Die Set — Steel block with roller bearing anvils (diam. = 0.22 in./5.5 mm).

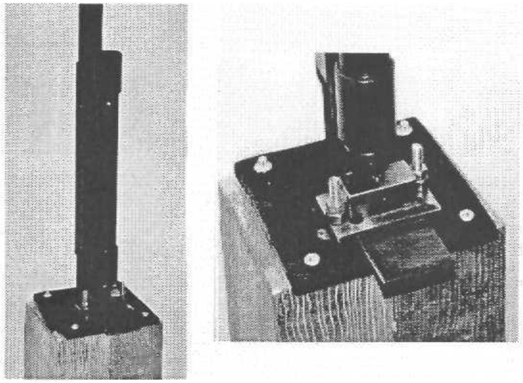
Drop-Hammer — Column and guide (square tubular steel).

— 2 kg drop-hammer (steel bar with replaceable end).

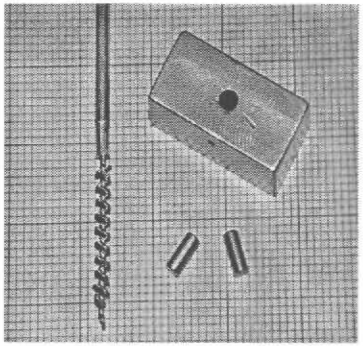
- Indication of ignition is any of the following: sparks, flash, snap, or smell of reaction products.

EXAMPLE OF IMPACT SENSITIVENESS APPARATUS

- Example of very simple and very inexpensive impact sensitiveness screening tester, shown in its 2 kg drop-hammer configuration. For 5 kg, an additional 3 kg weight is attached to its top.



- Die set, anvils and cleaning tool.



IMPACT SENSITIVENESS SCREENING PROCEDURE

- To determine the drop-hammer height necessary for approximately 50% ignitions:
  1) Begin testing with a hammer height of about 15 inches. Record whether there was an indication of ignition, using "+" for ignition or "0" for no ignition.
  2) For the next test, raise the drop height 3 in. for a "0" or lower the drop height 3 in. for a "+" result in the previous test.
  3) Repeat step 2 for a total of at least 30 trials.
  4) Record impact sensitivity (height) for the mixture as the height corresponding to that with approximately equal numbers of +'s and 0's.

- For example — for a 50:50 mixture of $KClO_4$ and S:

Impact Height	27"	24"	21"	18"	15"	12"
Results	+	+ 0	+ 0	+ 0	+ 0	0
		+	+ 0	+ 0	+ 0	0
		+	+ 0	+ 0	0	
			+	+ 0	0	
			+	+ 0	0	

Based on a quick examination of these results, ≈18" could be used as the 50% impact sensitivity. (However, a more complete mathematical analysis results in 19".)

IMPACT SENSITIVENESS SCREENING RANGES

- Somewhat arbitrarily, impact screening ranges have been established using 3 "standard" 50:50 binary mixtures. Using the above method, the heights corresponding to ignition 50% of the time must be established for each standard mixture.

S1	→	$KClO_3 + S$
S2	→	$KClO_4 + S$
S3	→	$KClO_3$ + Lactose

H_{S1}	≈	7"
H_{S2}	≈	19"
H_{S3}	≈	32"

- Accordingly, the following ranges were established.

H < 7"	→	Extraordinarily sensitive
7" < H < 19"	→	Very sensitive
19" < H < 32"	→	Sensitive
32" < H	→	Relatively insensitive

FLASH POWDER IMPACT SENSITIVITY

- **Flash powder I (previously discussed):**

Ingredient	Parts
Potassium chlorate	5
Antimony sulfide	1
Aluminum (German dark)	1

Exhibits a 50% impact sensitivity of 30", which falls in the "Sensitive" range.

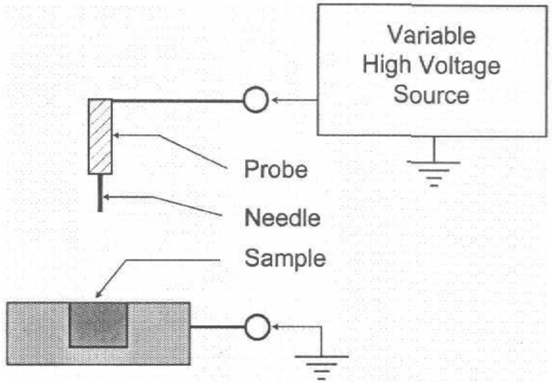
Height	33"	30"	27"
Results	+ 0	+ 0	0
	+	+ 0	0
	+	+ 0	0
	+	+ 0	0
			0

- **When 15% titanium (40–100 mesh) is added, its 50% sensitivity becomes ~15" (very sensitive), and it exhibits a much broader distribution.**

Height	24"	21"	18"	15"	12"	9"
Results	+	+ 0	+ 0	+ 0	+ 0	0
	+	+ 0	+ 0	+ 0	+ 0	0
		+	+ 0	+ 0	+ 0	0
			+	+ 0	0	

ELECTROSTATIC SENSITIVENESS

- **Electrostatic sensitiveness is a measure of a material's tendency to ignite in response to energy input as an electric spark.**



- **In one method, a sample is placed in a small well in an electrically grounded plate. A probe, connected *to a high voltage power source (usually a charged* capacitor), is brought toward the sample until a spark occurs, discharging through the sample.**

- **For a given apparatus, electrostatic sensitivity is reported as the electrical energy (in Joules) that results in ignition (for some specific percentage of trials). Because of differences in test methods, it is not unusual to find a range of values reported for the same pyrotechnic material.**

FLASH POWDER ELECTROSTATIC SENSITIVITIES

- **Flash mixtures and electrostatic 50% sensitivities** [Laib]:

Ingredients	1	2	3	4	5	6
Potassium perchlorate	30	67	—	64	—	67
Potassium chlorate	—	—	—	—	63	—
Barium nitrate	30	—	—	—	—	—
Black Powder	—	—	91	—	—	—
Aluminum	40	—	9	22	—	—
Aluminum (dark)	—	33	—	—	—	—
Antimony sulfide	—	—	—	4	32	—
Sulfur	—	—	—	10	—	—
Titanium	—	—	—	—	—	33
Gum Arabic	—	—	—	—	5	—
Electrostatic Sens. (J)	1.32	0.37	0.22	<0.1	<.05	.005

- **Note that Mix 6 is 264 times more sensitive than *Mix 1. Mix 2 and 4 are typical of those used in* fireworks salutes, and they produce essentially the same sound output. However, there is a factor of at least 4 in their sensitivity to electrostatic discharge.**

- **Metal powder particle size is an important factor in determining electrostatic sensitiveness. Unfortunately, this information was not available for the above data.**

ELECTROSTATIC ENERGY ON A PERSON

- **Electrostatic energy (in Joules) of a charged object is:**

$$E = \tfrac{1}{2} C V^2$$

where C = capacitance (in farads)
V = voltage (in volts)

- **For a large person C <500 pF (5×10^{-10} farad) and the maximum voltage to which a person can be charged is <20 kV (2×10^{4} volts) [Laib].**

- **Accordingly, the maximum electrostatic energy that a person can accumulate will be less than about 0.1 Joule (100 mJ).**

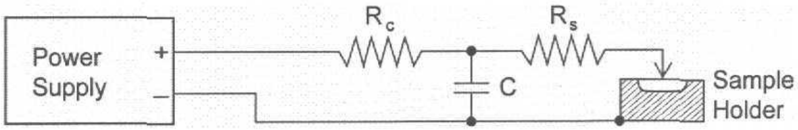
- **Discharges take place in less than ¼ microsecond.** [Bell]

- **Discharges of less then 3kV cannot be felt by a person.** [Bell]

- **Thus sparks less than about 2 mJ cannot be felt.**

ELECTROSTATIC SENSITIVENESS SCREENING APPARATUS

- Simple screening test apparatus:



- Power supply is at least 0 – 5 kV in 500 V steps. (100 V Steps preferred)

- R_s is a series resistance of 100 – 200 Ω, to extend the time of discharge and protect the capacitor, C. (like from a person)

- R_c is a charging resistance, chosen to limit the amount of added energy from the power supply during the discharge. It is adjusted for various values of C.

C (μF)	R_c (MΩ)	Charge Time (sec)
0.25	10	12
0.10	20	10
0.05	20	5
0.02	40	4

ELECTROSTATIC SENSITIVENESS SCREENING APPARATUS *(Continued)*

- The discharge probe must be shielded and heavily insulated for the operator's safety. (Always discharge capacitor before and while touching any circuit component.)

- The sample holder is an aluminum plate machined with a series of sample locations. Each sample location is about 1/4" (5 mm) across, rounding to a depth of about 1/16" (1 mm).
  - The samples are loaded by placing a small amount on the aluminum plate and using a thin scraper to move it into each sample location.
  - After all locations are filled flush with the surface, a single thickness of cellophane tape is used to seal the samples.

- After allowing time for the capacitor to charge, a test is conducted by placing the discharge probe (needle) against the tape over the sample. The instant the tip of the probe penetrates the tape, the discharge occurs.

ELECTROSTATIC SENSITIVENESS SCREENING APPARATUS (Continued)

- *Indication of ignition is any of the following:* sparks, flash, snap, tearing of the tape, or smell of reaction products.
- The discharge probe is cleaned after each test with fine grit emery paper and the sample holder is *cleaned after each test series.*
- Conduct a series of tests using the stair step method. When there is an ignition, decrease the voltage one step for the next test. When there is no ignition, increase the voltage one step for the next test.
- Continue testing for at least 30 trials.
  - Note that a change in the series resistance will change the results. Thus for comparisons, the series resistance must always be the same.

ELECTROSTATIC SENSITIVENESS SCREENING APPARATUS (Continued)

- *Record the ignition results for each trial in a table.* By inspection, estimate the voltage corresponding to approximately 50% ignitions.
- Example: Flash Powder, where C = 0.35 μF and R_s = 100 Ω

Voltage (kV)	6.0	5.5	5.0	4.5	4.0	3.5	3.0
Results	+	+ 0	+ 0	+ 0	+ 0	+ 0	0
		+	+ 0	+ 0	+ 0	0	
		+	+ 0	+ 0	+ 0	0	
			+	+ 0	0		
			+	+ 0			
			+				

50% Voltage ≅ 4.5 kV

50% Energy = 1/2 C V^2 = 3.5 J

FLASH POWDER ELECTROSTATIC SENSITIVITY

- Common flash powders:

Ingredient	III	IV	V
Potassium perchlorate	7	—	8
Potassium chlorate	—	7	—
Aluminum (Amer. Dark)	3	3	3
Antimony sulfide	—	—	2

- Electrostatic sensitivity:
  [C = 0.35 μF, R_s = 100 Ω]

Flash Powder	50% Sensitivity
III	7.4 J
IV	3.5 J
V	1.6 J

- Note: Sound levels of salutes made with these three formulations are all about the same.

BRUCETON COMPUTATIONS

- For screening tests, it is probably acceptable to simply look at the results and estimate the 50% stimulus level. However, the Bruceton Method may be used to calculate more accurate results.

- For the Bruceton Method:

  - Step sizes must be equal (and should be approximately equal to the expected standard deviation).

  - Use the stair step method (increase stimulus one step for non-ignitions and decrease one step for ignitions).

  - Record results from at least 30 trials and record the results.

  - For calculations, use the results for ignitions (+) or non-ignitions (0), whichever there were fewer. If the numbers are equal, use either (+ or 0).

BRUCETON COMPUTATIONS (Continued)

- Calculate 50% stimulus level using:

$$50\%\ \text{Stimulus} = S_L + S_S\,(A/N \pm \tfrac{1}{2})$$

where:

S_L = *Lowest stimulus level*

S_S = Stimulus step size

$A = \Sigma(i \bullet n_i)$

$N = \Sigma n_i$

[Use +½ if non-ignitions (0's) are used and –½ if ignitions (+'s) are used in the calculation.]

- For example: $KClO_4 + S$ impact data.

Stimulus Lowest to Highest	(n_i) No. of			
	+	0	i	i × n_i
12"	0	2	0	0
15"	2	5	1	2
18"	5	5	2	10
21"	5	3	3	15
24"	3	1	4	12
27"	1	0	5	5
Sums	16	16	—	44

↑ Using +'s

$$50\%\ \text{Stimulus} = 12 + 3(44/16 - \tfrac{1}{2}) = 18.75$$

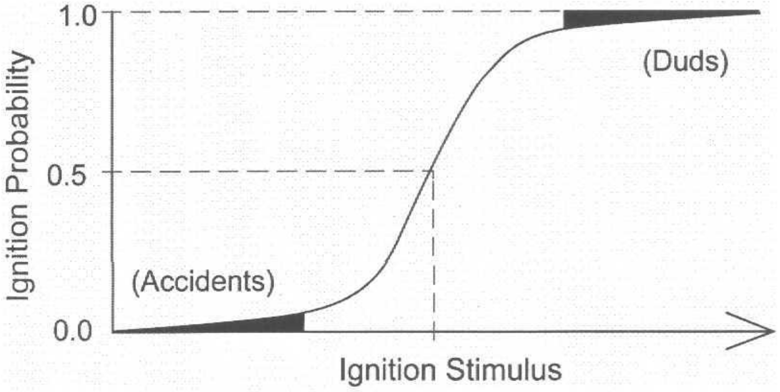
CAUTIONS ABOUT SENSITIVENESS INDICATORS

- The sensitiveness of a composition is almost impossible to predict; it should be measured. Sensitiveness will depend on things such as:
  - Particle size.
  - Temperature.
  - Impurities.
  - Crystal form.
  - Humidity.
- Sensitiveness cannot be predicted from one indicator to another. Each one should be measured.
- Sensitiveness values are highly subjective. They depend on things such as the:
  - Apparatus used.
  - Test method.
  - Sample preparation.
  - Individual doing the tests.

PROBABILITY VS STIMULUS

- **A probability of 0.0 means something never happens, ever. A probability of 1.0 means something always happens, every time.**

- **Ignition probabilities are essentially never 0 or 1, but always somewhere in between. When plotted against ignition stimulus, they produce the so-called S-curve (Sigmoid curve).**

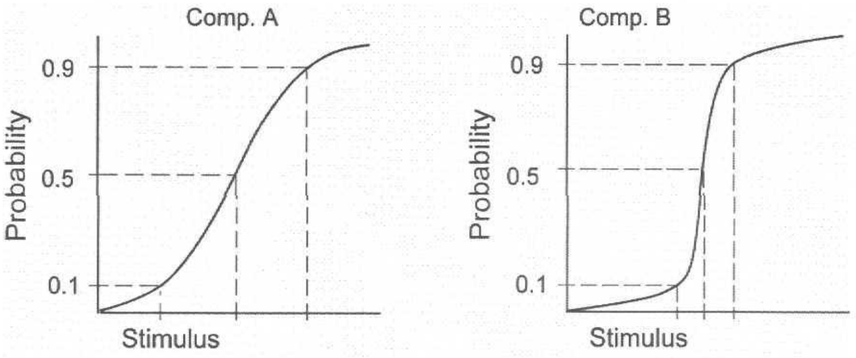


- **That the probability for ignition never quite goes to 0.0 means that there is always a chance for accidental ignition with any handling of a pyrotechnic material.**

PYROTECHNIC SENSITIVITY

- **Pyrotechnic sensitivity is often given as the level of stimulus that results in ignition in some percentage of trials. Often the 50% value is reported, but sometimes it is the 10% value or even the 1% value may be reported. In comparing data, it is essential to know which level is being reported.**

- **It can also be very important to know how rapidly the ignition probability changes as a function of ignition stimulus.**



- **The 50% ignition stimulus is the same for both composition A and B. However, A is much less predictable, and it is much more likely that there will be duds and accidental ignitions with composition A.**

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SECTION 12

PYROTECHNIC HAZARD MANAGEMENT

- Elements of Hazard Management
- Chemical Toxicity Hazards
- Pyrotechnic Hazards
- Hazardous Chemical Combinations
- Control of Hazards

SAFETY CONCERNS

- There are three areas of concern regarding safety for anyone studying, researching or making pyrotechnics.
  - Public Safety — It is simply unacceptable to allow any member of the public to be placed at risk because of your activities. (For hobbyists, this includes your minor children and non-participating adult family members.)
  - Personal Safety — Serious injury to yourself or other participating adults will be widely reported to the discredit of everyone associated with pyrotechnics. (You may have the right to injure yourself, but you have an obligation to your peers, not to do so.)
  - Property Damage — As above.
- If you work with pyrotechnics long enough, you WILL have an accident. It is essential that you take the steps NOW to make certain it is a very rare event and that it is only a small and relatively inconsequential accident.

SAFETY

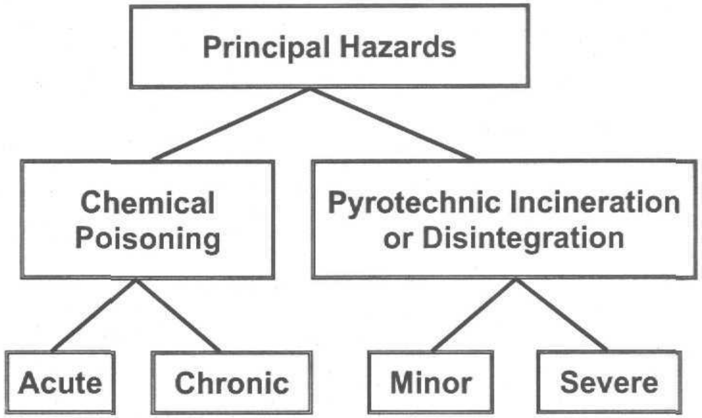
- Dictionary definition of "safe":
  - "Involving no risk of mishap, error, etc."
- By this (poor) definition of safe, nothing mankind does is safe because there is always some "risk of mishap" in literally every possible activity.
  - Crossing street → Being hit by a car.
  - Eating food → Choking or food poisoning.
  - Reading a book → Getting a paper cut.
- Definition of "safe" from hazard management:
  - "Something is safe when the attendant risks are below an acceptable level". (This is the definition we shall use.)

HAZARD MANAGEMENT

- Elements of hazard management for experimentation and manufacturing of pyrotechnics:
  - Recognition — is gained by understanding how pyrotechnics function and knowledge of pyrotechnic sensitiveness.
  - Evaluation — is the process of estimating the probability and consequences of accidents.
  - Control — is taking the actions to reduce the probability and consequences of accidents.
- Pyrotechnic materials are not excessively dangerous when they are properly handled and used. Most accidents are the result of carelessness.
- Each year people are needlessly injured (or killed) because of failures to recognize and take seriously the potential dangers from pyrotechnic materials.

RECOGNITION OF HAZARDS IN PYROTECHNICS

- Hazards in pyrotechnics generally fall into two areas, toxic chemical effects and the results of accidental (or ill-considered) ignition.



Examples	Cause	Consequence
Acute poisoning	Inhalation of barium nitrate dust	Diarrhea
Chronic poisoning	Inhalation of potassium dichromate dust	Lung cancer
Minor incineration	Star throwing	Burnt fingers
Major disintegration	Explosion and fire during manufacture	Dismemberment, 3rd degree burns

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CHEMICAL (TOXIC) HAZARDS

- Acute Poisoning — A fairly immediate response to a toxic substance. Generally, treatment is sought immediately, because the person is obviously sick, and unless the exposure is massive, there is a high probability of survival.

- Chronic Poisoning — A delayed response (weeks to years) to exposure to toxic substances. Generally, treatment is sought long after the damage has been done and too often the prognosis is grim.

  - Some chemicals to take great care with:

Cumulative poisons	Cancer suspect agents
Arsenic compounds	Arsenic compounds
Lead compounds	Azo dyes
Mercury compounds	Dichromates
Thallium compounds	Nickel compounds
	Thiourea
	Hexachloroethane
	Hexachlorobenzene
	Benzene hexachloride

SAFETY RATING SYSTEM FOR PYRO-CHEMICALS

- The following hazard ratings are generally those assigned by J.T. Baker, Inc. (a major supplier of laboratory chemicals). Safety ratings range from 0 to 4, expressing the following hazard level:

  0 = None,
  1 = Slight,
  2 = Moderate,
  3 = Severe, and
  4 = Extreme.

- Safety ratings in four areas of hazard concern are:

  H = Health is the danger or toxic effect a substance presents if inhaled, ingested, or absorbed,
  F = Flammability is the tendency of the substance to burn,
  R = Reactivity is the potential of a substance to explode or react violently with air, water or other substances, and
  C = Contact is the danger a substance presents when exposed to skin, eyes, and mucous membranes.

- In using the safety rating information, it is important to understand that the ratings are for unmixed chemicals only. It must be understood that mixtures may have significantly different health and safety characteristics which may not be predictable. Further, pyrotechnic mixtures will certainly have significantly greater flammability characteristics and can often react explosively.

SAFETY RATINGS FOR PYROCHEMICALS

Description	H	F	R	C
Accroides resin (red gum)	1	2	0	1
Acetone (solvent)	1	3	2	1
Aluminum (400 mesh, flake)	1	4	2	1
Aluminum (325 mesh, granular)	1	3	2	1
Ammonium dichromate	4	1	3	3
Ammonium nitrate	1	0	3	2
Ammonium perchlorate	1	0	3	2
Anthracene	1	1	0	1
Antimony sulfide (325 mesh)	3	3	2	1
Barium carbonate	2	0	0	1
Barium chlorate	3	0	3	1
Barium nitrate	3	0	3	1
Barium sulfate	1	0	0	0
Benzene	4	3	2	1
Boric acid	2	0	0	2
Cab-o-sil (Colloidal silica)	2	0	0	1
Calcium carbonate	0	0	0	1
Calcium sulfate	1	0	0	1
Charcoal (80 mesh)	0	1	0	1
Charcoal (air float)	0	2	0	1
Chlorowax	2	1	1	1
Clay (Bentonite, very fine powder)	1	0	0	0
CMC (Sodium carboxymethylcellulose)	1	1	1	1
Copper(II) carbonate (basic)	2	0	0	1
Copper(II) oxide (black, cupric)	2	0	0	1
Copper(II) oxychloride	2	0	0	1
Copper(II) sulfate (cupric)	2	0	0	2
Cryolite	1	0	0	1
Dechlorane	2	1	1	2
Dextrin (yellow)	0	1	0	0
Gallic acid, monohydrate	1	1	0	1
Graphite (325 mesh)	1	2	0	0
Hexachlorobenzene (HCB)	2	1	1	1
Hexachloroethane (HCE)	2	1	1	1
Hexamine (Hexamethylene-tetraamine)	1	1	1	1
Hydrochloric acid (concentrated)	3	0	2	3

SAFETY RATINGS FOR PYROCHEMICALS (Cont.)

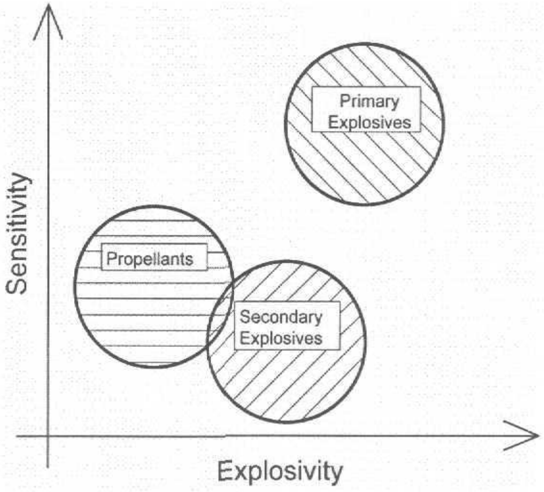
Description	H	F	R	C
Iodine, sublimed	3	0	2	3
Iron oxide (black, ferrosoferic)	1	0	1	1
Iron (III) oxide (red)	1	0	1	1
Isopropanol (Isopropyl alcohol)	1	3	1	1
Lactose	0	1	1	0
Lampblack (oil free)	1	2	0	1
Lead, granular	3	0	0	1
Lead dioxide	3	0	3	1
Lead nitrate	3	0	3	1
Lead oxide (red, minium)	3	0	1	1
Magnesium (200 mesh)	1	3	2	0
Magnesium (325 mesh)	1	4	2	0
Magnesium alum. 50/50 (granular, 100-200 mesh)	1	3	2	1
Magnesium alum. 50/50 (granular, 200-400 mesh)	1	4	2	1
Magnesium carbonate	1	0	1	0
Manganese dioxide	1	0	1	1
Methanol (Methyl alcohol)	3	3	1	1
Methylene chloride	3	1	1	2
Mineral oil	1	1	0	1
Nitric acid (concentrated)	3	0	3	4
Nitrocellulose (Lacquer, 10% solution)	1	3	2	1
Paraffin oil	1	1	0	1
Parlon (chlorinated natural rubber)	2	1	1	1
Phosphorus, red	0	2	2	2
Picric acid, crystal	2	2	2	2
Polyvinyl chloride (PVC)	2	1	1	1
Potassium, lump	3	3	3	4
Potassium bicarbonate	1	0	1	0
Potassium chlorate	1	0	3	2
Potassium dichromate (fine granular)	4	0	3	3
Potassium hydroxide, pellets	3	0	2	4
Potassium nitrate	1	0	3	2
Potassium perchlorate	1	0	3	2
Potassium permanganate	2	0	3	2
Potassium sulfate	1	0	0	0
PVC (Polyvinyl chloride)	2	1	1	1

SAFETY RATINGS FOR PYROCHEMICALS (Cont.)

Description	H	F	R	C
Red gum (Accroides resin)	1	2	0	1
Shellac (-120 mesh, orange)	1	2	0	1
Silica (fumed-colloidal, Cabosil)	2	0	0	1
Silica gel (60-200 mesh)	2	0	0	1
Silicon powder (325 mesh)	2	3	1	1
Silver nitrate, crystal	3	0	3	3
Smoke dye	1	1	1	2
Sodium, lump	3	3	3	4
Sodium azide	3	2	3	2
Sodium benzoate	1	1	0	1
Sodium bicarbonate	0	0	1	1
Sodium carboxymethylcellulose (CMC)	1	1	1	1
Sodium chlorate, crystal	1	0	3	1
Sodium cyanide, granular	3	0	2	3
Sodium hydroxide, pellets	3	0	2	4
Sodium nitrate	1	0	3	1
Sodium oxalate	3	0	1	2
Sodium salicylate	1	1	0	1
Sodium silicate (water glass, liquid)	1	0	0	2
Sodium sulfate	0	0	0	1
Starch, soluble potato	0	1	0	1
Stearic acid	1	1	1	1
Strontium carbonate	1	0	0	1
Strontium nitrate	1	0	3	1
Strontium sulfate	1	0	0	1
Sulfur (flour)	1	1	0	1
Sulfuric acid (concentrated)	3	0	3	4
Talc, powder	1	0	0	1
Tetrachloroethane	3	0	1	2
Tin, granular (20 mesh)	0	0	0	1
Titanium metal powder (100 mesh)	1	3	2	1
Titanium metal powder (300 mesh)	1	4	2	1
Titanium tetrachloride	3	0	2	3
Trichloroethylene (stabilized)	3	1	2	2
Water	0	0	1	0
Zinc metal powder (dust)	1	3	2	1
Zinc oxide	2	0	0	0

PYROTECHNIC HAZARDS

- **Pyrotechnic hazards include both incendiary and explosive output, and most often result from accidental ignitions.**
- **Some types of explosives have sensitivities (to accidental ignition) that tend to fall into fairly well defined regions, and their output is also fairly predictable.**



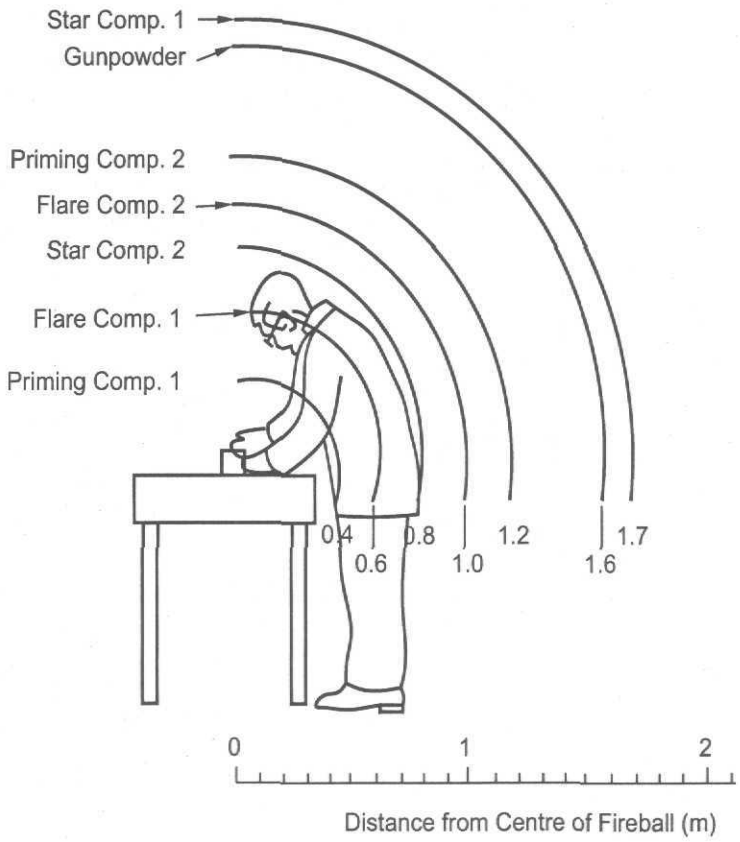
- **Pyrotechnic materials can be found throughout much of the same range of sensitivity and explosivity. Thus prediction of pyrotechnic hazards is much more difficult.**

HAZARDS FROM BURNING

- **Thermal Effects — High temperatures are produced (300 – 3500 °C) and may be sustained for relatively long periods of time, thus severe burns and incendiary effects are likely.**
- **Pressure Effects — There is no rise above atmospheric pressure, thus there will be no pressure effects unless the material is confined. Then the blast effect will be from mechanical rupturing of the pressure vessel.**
- **If burn type transitions occur (discussed earlier), thermal output can be greatly multiplied, and further transition to deflagration or even detonation may be possible.**

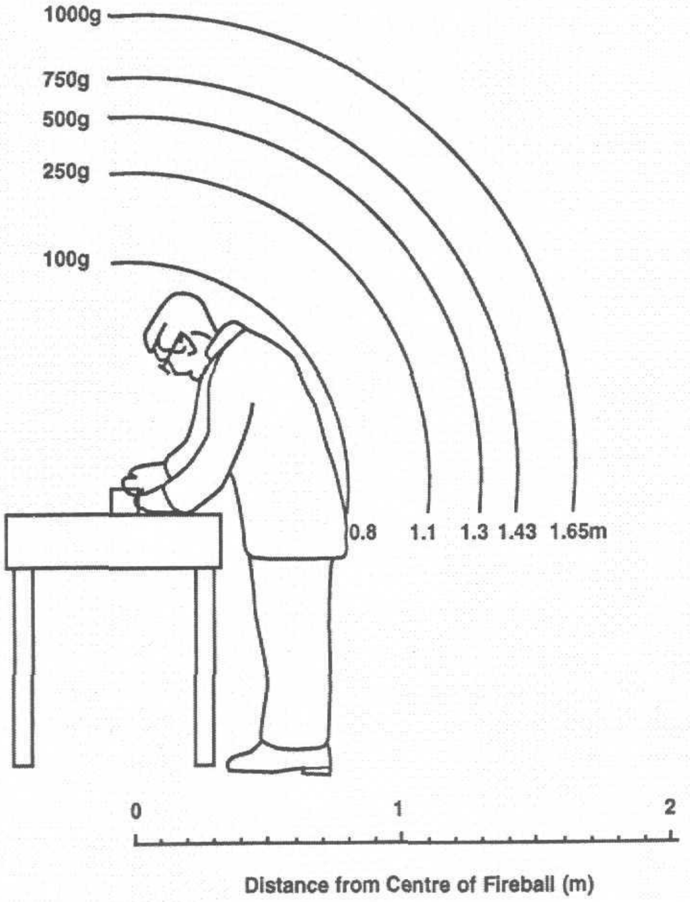
FIREBALL SURVIVABILITY

- **As a very general rule, being within the range of a fireball from burning pyrotechnic compositions, in normal clothing, will be fatal in about half the cases. For 1 kg (2.2 lb) of composition, the expected fireball radii are as shown.**



FIREBALL SURVIVABILITY (Continued)

- **For various amounts of Black (gun) Powder, the expected fireball radii are as shown.**



HAZARDS FROM DEFLAGRATIONS

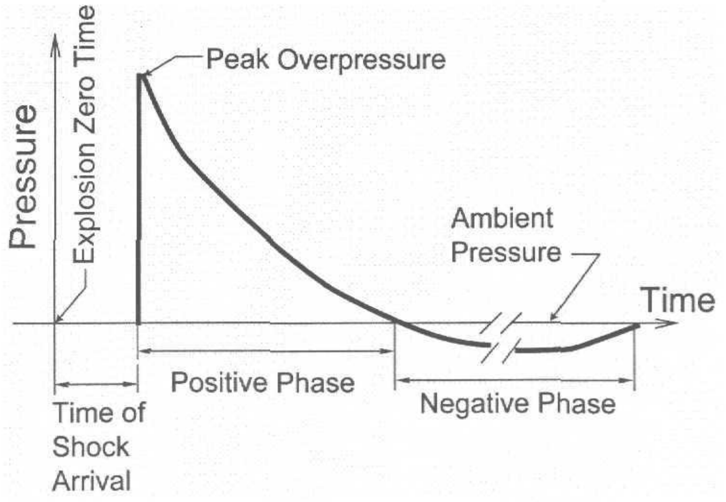
- Pressure Effects — High local pressures can be produced (100 – 10^4 psi). However, when confined, much of the blast effect is the result of sudden mechanical rupturing of the pressure vessel, which will generally produce fragments.
    - → Near contact with the explosive:
        - — Heaving Effects, although relatively low strength materials (such as wood and glass) can be broken into many pieces.
    - → Separated from the explosive:
        - — Blast Effects, indistinguishable from those produced by an "equivalent" *weight of detonating explosive.*
- Thermal Effects — Somewhat higher temperatures are produced than burning (1500 – 4000 °C). However, they are sustained for much shorter periods. Thus, while (flash) burns and incendiary effects are possible, they will be much less severe than for burning.

HAZARDS FROM DETONATIONS

- Pressure Effects — Incredibly high local pressures are produced (10^5 to $5\text{x}10^6$ psi). Pressure effects are mostly independent of any confinement.
    - → Near contact with the explosive:
        - — Shattering Effects, even in high strength materials (rock and steel).
    - → Separated from the explosive:
        - — Blast Effects, as the result of the passage of a pressure wave.
        - — Impact Effects, from locally produced projectiles.
- Thermal Effects — Even higher temperatures are generated (2000 – 4000 °C) but persist for such a short time as to be insignificant in comparison with pressure effects.

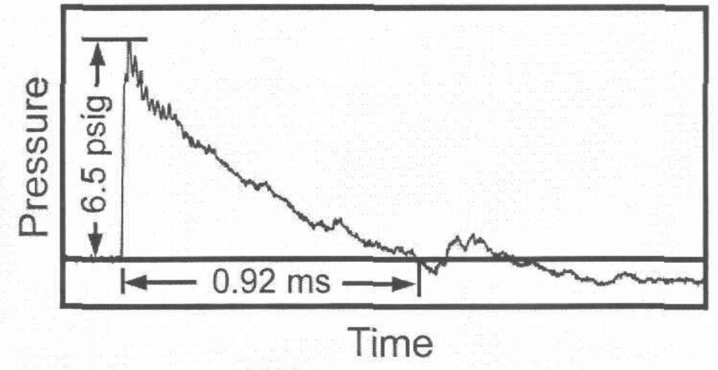
BLAST WAVE STRUCTURE

- **Blast (Shock) Waves are produced by all explosions, although they quickly degenerate into sound waves.**
- **In air, blast waves propagate at speeds at least a little in excess of the speed of sound (≈330 m/sec). Thus there is no audible precursor to the arrival of a blast wave, which produces a near instantaneous rise in local pressure. Then there is a decay of pressure back to ambient. Following this positive phase, there is a negative phase during which the pressure falls below ambient.**



BLAST WAVE STRUCTURE (Continued)

- **Accompanying the pressure changes are changes in air motion. During the positive phase, there is net air motion away from the explosion. During the negative phase, net air motion reverses.**
- **Blast wave recorded for a fireworks test salute, 50 g of flash powder [70:30, potassium perchlorate: aluminum (German dark)].**



BLAST DAMAGE

- ***Damage from blast waves with very long duration*** **positive phase (≈ 1 sec). This would be from very large explosions, a large distance away (thousands of pounds at thousands of feet).**

Type of Damage [Kinney & Graham]	Peak Overpressure (psi)
Typical window glass breakage	0.1 – 0.2
Windows shattered, plaster cracked; minor damage to some buildings	0.5 – 1.0
Personnel knocked down	1.0 – 1.5
Failure of walls constructed of concrete blocks or cinder blocks	1.9 – 3.0
Self-framing paneled buildings collapse	3.0 – 4.5
Eardrum rupture	5 – 15
Railroad cars overturned	6 – 9
Lung damage	30 – 75
Lethality	100 – 200
Crater formation in average soil	300 – 450

SOME HAZARDOUS CHEMICAL COMBINATIONS

- ***Some combinations that can be particularly*** **hazardous are listed in the matrix below. However, the list is not all inclusive and on occasion some listed combinations may not present a high degree of hazard.**

	Chlorates	Perchlorates	Aluminum	Magnesium	Zinc
ClO_3^-	O	(1)	X(2,3)	X(2,3,4)	X(2,3,4)
ClO_4^-	(1)	O	?(2)	?(2,4)	—
Al	X(2,3)	?(2)	O	—	—
Mg	X(2,3,4)	?(2,4)	—	O	—
Zn	X(2,3,4)	—	—	—	O
Acids	X(5)	—	—	X(6)	X(6)
NH_4^+	X(8)	—	—	X(8)	X(8)
Water	—	—	?(7)	X(7)	X(7)
Cu^{2+}	?(9	—	?(10)	X(10)	X(10)
S	X(11)	X(11)	—	X(12)	X(12)
S^{2-}	X(11)	X(11)	—	—	—

X = Generally hazardous combination
? = Can be hazardous depending on circumstances
— = Minimal hazard
O = Place filler

- **See following pages for explanation of the numbered notes.**

SOME HAZARDOUS COMBINATIONS (Continued)

- Notes for matrix:
    1) The specific combination of potassium chlorate and ammonium perchlorate can produce highly unstable ammonium chlorate, if moisture is present.
    2) Oxidizers in combination with metal fuels produce highly energetic mixtures. If the metal is a fine powder, the mixtures can be powerfully explosive. Also metal fuels tend to make mixtures more electrostatic sensitive.
    3) Chlorates have particularly low activation energy barriers, tending to make mixtures that are sensitive to all types of accidental ignition.
    4) Unprotected active metals can react with oxidizers to produce heat.
    5) *The presence of an acid tends to cause chlorates to* decompose, which sensitizes the mixture and can cause spontaneous ignition.
    6) Unprotected active metals react violently with acids producing heat and hydrogen gas. This can lead to spontaneous ignition and explosions.

SOME HAZARDOUS COMBINATIONS (Continued)

- Notes for matrix (Continued):
    7) Unprotected active metals react slowly with water to produce heat and hydrogen gas. With increasing temperature the reaction can become violent. This can lead to spontaneous ignition and explosions.
    8) Ammonium ions are capable of acting as an acid (so-called proton donor) potentially leading to the hazards outlined in Note 4 (chlorates) and Note 5 (active metals).
    9) Copper ions are capable of catalyzing the decomposition of some oxidizers. If that oxidizer is already somewhat unstable, it is possible to create mixes that are particularly sensitive to accidental ignition.
    10) Metals more active (electrochemically) than copper will react with copper ions to produce copper metal and active metal ions. This “displacement” reaction is exothermic, which increases the chance of spontaneous displacement ignition.
    11) Sulfur and sulfides, in combination with perchlorates and particularly with chlorates, form mixes that are sensitive to accidental ignition.
    12)`Sulfur can act as an oxidizer, as well as a fuel. When in combination with an unprotected active metal fuel, sulfur can attack it, producing heat.

HAZARDS OF COMBINATION — EXAMPLE

- As an exercise, regarding hazardous combinations of chemicals, consider what is wrong with this proposed blue star formulation?

Ingredient	%
Ammonium perchlorate	30
Potassium chlorate	30
Sulfur	20
Copper(II) sulfate	10
Zinc	10

(Dampen with water.)

- Literally, everything!!!

See previous notes for hazardous chemical combinations:

1	2	3
6	7(4, 5)	8
9	10	11
12		

HAZARD CONTROL

- Hazard evaluation has two components:
  - Probability of occurrence.
  - Consequence of occurrence.
  - A minor hazard has either a low probability or minimal consequence.

Activity	Consequence	Probability	Risk
Jumping off tall buildings to see if you can fly.	Crash landing. (Severe)	Very High. (≈100%)	Unacceptable.
Swimming in the sea.	Eaten by sharks. (Severe)	Very Low. (≈0%)	Acceptable.
Flipping a coin to decide which movie to see.	The other movie is better. (Inconsequential)	High. (50%)	Acceptable.

- Hazards are least when both the probability is low and the consequences are minor.

CONTROLLING TOXIC HAZARDS

- **Probability minimization:**
  - *Learn which chemicals have particularly high* health and contact hazard ratings.
  - Whenever practical, avoid the use of chemicals with high health and contact hazard ratings. When roughly equivalent results can be achieved, use only those chemicals with low hazard ratings.
- *Consequence minimization:*
  - Use a well-fitting face (breathing) mask rated for "toxic dusts". Masks rated for "nuisance dusts" are better than nothing but do not offer sufficient protection. If there is significant dust in the air, the mask should cover the eyes, as well.
  - Operate in a manner such that dusts are not *created or are drawn away from personnel with* air handling equipment.

CONTROLLING TOXIC HAZARDS (Continued)

- **Consequence minimization (Continued):**
  - *Change outer clothing at least daily and* thoroughly wash (shower) at the end of work.
  - Clean up spills immediately. Sweep and wash work surfaces and equipment frequently during the day. Sweep the floor at least once a day. Totally clean the area at least once a week.
  - Do not eat or drink (or smoke) in the work area; *and wash face and hands before eating or* drinking (or smoking).
  - Wear plastic (rubber) gloves and an apron when exposure is prolonged or if contact hazard is high.
  - Have eye wash equipment available. (A quart bottle filled with clean water may be minimally adequate.)

CONTROLLING PYROTECHNIC HAZARDS

- Probability minimization:
  - A study of incidents involving the accidental ignition of pyrotechnics finds that about 70% are the result of friction [McIntyre].
  - Know the sensitivity of all compositions used.
    - Avoid the most sensitive where possible.
    - Take added precautions where not possible.
  - Control Friction Sensitiveness.
    - Include phlegmatizers (lubricants) in formulations.
    - Never scrape dried composition or slide containers.
    - Monitor clearances in mixers.
  - Control Impact Sensitiveness.
    - Use soft and non-sparking tools and work surfaces.
    - Press slowly, rather than ramming (hammer blows).

CONTROLLING PYROTECHNIC HAZARDS (Cont.)

- Probability Minimization (Continued):
  - Control Auto-Ignition Sensitiveness.
    - No open flame or high temperature heating equipment in work areas.
    - Avoid producing pyrotechnic dust in areas around motor vehicles (hot exhaust systems).
    - Keep bearings clean and lubricated.
  - Control Electrostatic Sensitiveness.
    - Control static buildup (materials, dissipatives).
    - Ground equipment.
    - Provide means of safely discharging personnel.
  - Control Chemical Sensitiveness.
    - Monitor for adverse reactions (heat or smell).
    - Consider non-aqueous binders.

CONTROLLING PYROTECHNIC HAZARDS (Cont.)

- Probability Minimization (Continued):
  - Other Strategies:
    - = Use proper tools and work areas.
    - = Keep tools, work surfaces and floors clean.
    - = Work at a measured pace rather than rush.
    - = Don't work when tired or distracted.
    - = Think, plan activities in advance.
    - = When in doubt, DON'T!
    - = When not in doubt, Think Twice!

CONTROLLING PYROTECHNIC HAZARDS (Cont.)

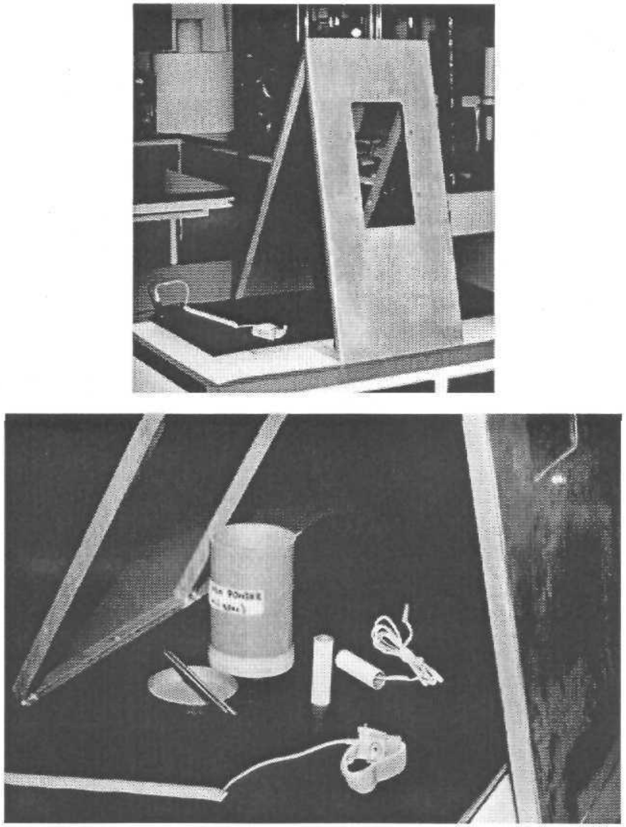
- Consequence Minimization:
  - Personal protection equipment can be useful in limiting the effects from minor fire and explosion.
    - = Face shield.
    - = Leather apron.
    - = Fire-resistant clothing.
    - = Leather, Kevlar, or steel mesh gloves.
    - = Hearing protection.
    - = Work shields.
  - No amount of personal equipment will offer significant protection in the event of a major fire or explosion.
    - = Remote operations.

CONTROLLING PYROTECHNIC HAZARDS (Cont.)

- Consequence Minimization (Continued):
  - Other strategies:
    - = Use minimum quantities of materials.
    - = Cover exposed composition.
    - = Remove and store completed items.
    - = Use safety shields and operate remotely.
    - = Separate workers and work areas.
    - = Never work completely alone.
    - = No unnecessary persons in immediate work area.
    - = Easy, *short and direct exits from work areas.*
    - = Provide explosion venting.

EXAMPLE OF SAFETY SHIELD

- For many materials, especially in small amounts, even a thin steel sheet with a polycarbonate window affords substantial protection for the face and body of a technician.



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PERIODIC TABLE OF THE ELEMENTS

Table of Selected Radioactive Isotopes

$_{0}$n	1	(15.3 min) β^-
$_{1}$H	3	(12.26 y) β^-
$_{4}$Be	7	(53.3 d) EC
	10	(1.6×10^6 y) β^-
$_{6}$C	11	(20.40 min) β^+
	14	(5730 y) β^-
$_{9}$F	18	(109.8 min) β^+
$_{11}$Na	22	(2.602 y) β^+, EC
	24	(15.02 h) β^-
$_{12}$Mg	28	(20.9 h) β^-
$_{13}$Al	26	(7.2×10^5 y) β^+, EC
$_{15}$P	32	(14.26 d) β^-
$_{16}$S	35	(87.2 d) β^-
$_{17}$Cl	36	(3.01×10^5 y) β^-
	38	(37.2 min) β^-
$_{18}$Ar	37	(35.02 d) EC
	39	(265 y) β^-
$_{19}$K	40	(1.28×10^9 y) EC
	42	(12.36 h) β^-
$_{20}$Ca	45	(165 d) β^-
$_{21}$Sc	46	(83.80 d) β^-
$_{24}$Cr	51	(27.70 d) EC
$_{25}$Mn	53	(2×10^6 y) EC
	54	(313.0 d) EC
	56	(2.578 h) β^-
$_{26}$Fe	59	(44.6 d) β^-
$_{27}$Co	56	(78.8 d) β^+, EC
	57	(270 d) EC
	58	(71.3 d) β^+, EC
	60	(5.272 y) β^-
$_{28}$Ni	57	(36.0 h) β^+, EC
	59	(8×10^4 y) EC
	63	(92 y) β^-
$_{29}$Cu	64	(12.70 h) β^-, β^+, EC
	67	(61.88 h) β^-
$_{30}$Zn	65	(244.1 d) β^+, EC
$_{31}$Ga	67	(78.2 h) EC
	72	(14.10 h) β^-
$_{32}$Ge	68	(275 d) EC
$_{33}$As	73	(80.3 d) EC
	74	(17.9 d) β^-, β^+, EC
$_{34}$Se	75	(118.5 d) β^-
	79	(6.5×10^4 y) β^-
$_{35}$Br	82	(35.34 h) β^-
$_{36}$Kr	81	(2.1×10^5 y) EC
	85	(10.72 y) β^-
$_{37}$Rb	86	(18.7 d) β^-
	87	(4.8×10^{10} y) β^-
$_{38}$Sr	90	(28.8 y) β^-
$_{39}$Y	88	(106.6 d) β^+, EC
$_{40}$Zr	93	(1.5×10^6 y) β^-
	95	(64.0 d) β^-
$_{41}$Nb	94	(2.0×10^4 y) β^-
	95	(35.15 d) β^-
$_{42}$Mo	99	(66.02 h) β^-
$_{43}$Tc	97	(2.6×10^6 y) EC
	98	(4.2×10^6 y) β^-
	99	(2.13×10^5 y) β^-
$_{44}$Ru	106	(367 d) β^-
$_{45}$Rh	101	(3.3 y) EC
$_{46}$Pd	103	(17.0 d) EC
	107	(7×10^6 y) β^-
$_{47}$Ag	108	(127 y) EC
	110	(252 d) β^-
	111	(7.45 d) β^-
$_{48}$Cd	109	(453 d) EC
$_{49}$In	114	(49.51 d) IT
$_{50}$Sn	121	(76 y) β^-
$_{51}$Sb	124	(60.20 d) β^-
	125	(2.7 y) β^-
$_{52}$Te	121 m	(154 d) IT
	123 m	(119.7 d) IT
	127 m	(109 d) IT
$_{53}$I	129	(1.6×10^7 y) β^-
	131	(8.040 d) β^-
$_{54}$Xe	133	(5.25 d) β^-
	135	(9.10 h) β^-
$_{55}$Cs	134	(2.06 y) β^-
	135	(2.9×10^6 y) β^-
	137	(30.17 y) β^-
$_{56}$Ba	140	(12.8 d) β^-
$_{57}$La	137	(6×10^4 y) EC
	140	(40.3 h) β^-
$_{58}$Ce	144	(284 d) β^-
$_{59}$Pr	142	(19.1 h) β^-
$_{60}$Nd	147	(11.1 d) β^-
$_{61}$Pm	145	(18 y) EC
	147	(2.62 y) β^-
$_{62}$Sm	146	(7×10^7 y) α
	151	(93 y) β^-
$_{63}$Eu	152	(13 y) β^+, EC, β^-
	154	(8.5 y) β^-
$_{64}$Gd	150	(2.1×10^6 y) α
$_{65}$Tb	158	(1.2×10^3 y) EC, β^-
	160	(72.3 d) β^-
$_{67}$Ho	166 m	(1.2×10^3 y) β^-
$_{69}$Tm	170	(128.6 d) β^-
	171	(1.92 y) β^-
$_{70}$Yb	169	(32.0 d) EC
	175	(4.19 d) β^-
$_{71}$Lu	176	(3.7×10^{10} y) β^-
$_{73}$Ta	182	(115.0 d) β^-
$_{74}$W	181	(140 d) EC
	185	(75.1 d) β^-
	188	(69 d) β^-
$_{75}$Re	187	(5×10^{10} y) β^-
$_{76}$Os	194	(6.0 y) β^-
$_{77}$Ir	192	(74.2 d) β^-, β^+, EC
$_{79}$Au	195	(183 d) EC
	196	(6.18 d) β^+, EC, β^-
	198	(2.696 d) β^-
	199	(3.15 d) β^-
$_{80}$Hg	203	(46.8 d) β^-
$_{81}$Tl	204	(3.77 y) β^-
$_{82}$Pb	202	(3×10^5 y) EC
	205	(3×10^7 y) EC
	210	(22.3 y) β^-, α
$_{83}$Bi	207	(38 y) EC
	208	(3.7×10^5 y) EC
	210	(5.01 d) β^-, α
	210 m	(3×10^6 y) α
$_{84}$Po	208	(2.90 y) α
	209	(102 y) α
	210	(138.38 d) α
$_{85}$At	209	(5.4 h) EC, α
	210	(8.1 h) EC
	211	(7.21 h) EC, α
$_{86}$Rn	222	(3.824 d) α
$_{87}$Fr	212	(19.3 min) EC, α
	222	(15 min) β^-
	223	(21.8 min) β^-
$_{88}$Ra	226	(1.60×10^3 y) α
$_{89}$Ac	227	(21.77 y) β^-
$_{90}$Th	228	(1.913 y) α
	230	(7.7×10^4 y) α
	232	(1.40×10^{10} y) α
$_{91}$Pa	231	(3.28×10^4 y) α
$_{92}$U	233	(1.59×10^5 y) α
	234	(2.44×10^5 y) α
	235	(7.04×10^8 y) α
	236	(2.34×10^7 y) α
	238	(4.47×10^9 y) α
$_{93}$Np	236	(1.1×10^5 y) EC, β^-
	237	(2.14×10^6 y) α
	239	(2.346 d) β^-
$_{94}$Pu	238	(87.75 y) α
	239	(2.41×10^4 y) α
	240	(6.54×10^3 y) α
	242	(3.8×10^5 y) α
	244	(8.3×10^7 y) α
$_{95}$Am	241	(432 y) α
	243	(7.37×10^3 y) α
$_{96}$Cm	242	(163.2 d) α
	244	(18.12 y) α
	247	(1.55×10^7 y) α
	248	(3.5×10^5 y) α, SF
$_{97}$Bk	247	(1.4×10^3 y) α
$_{98}$Cf	249	(351 y) α
	251	(900 y) α
$_{99}$Es	252	(472 d) α
	253	(20.47 d) α
	254	(276 d) α
$_{100}$Fm	255	(20.1 h) α
	257	(100.5 d) α
$_{101}$Md	258	(55 d) α
$_{102}$No	259	(58 min) α
$_{103}$Lr	260	(3.0 min) α
$_{104}$Rf	261	(65 s) α
$_{105}$Db	262	(40 s) α
$_{106}$Sg	263	(0.9 s) α

Selected Radioactive Isotopes

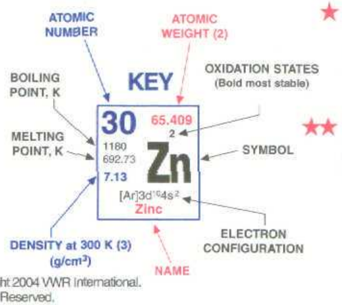
Naturally occurring radioactive isotopes are designated by a mass number in blue (although some are also manufactured). Letter m indicates an isomer of another isotope of the same mass number. Half-lives follow in parentheses, where s, min, h, d, and y stand respectively for seconds, minutes, hours, days, and years. The table includes mainly the longer-lived radioactive isotopes; many others have been prepared. Isotopes known to be radioactive but with half-lives exceeding 10^{12} y have not been included. Symbols describing the principal mode (or modes) of decay are as follows (these processes are generally accompanied by gamma radiation):

α	alpha particle emission
β^-	beta particle (electron) emission
β^+	positron emission
EC	orbital electron capture
IT	isomeric transition from upper to lower isomeric state
SF	spontaneous fission

GROUP 1/IA	2/IIA	3/IIIA	4/IVA	5/VA	6/VIA	7/VIIA	8	9 VIIIA	10	11/IB	12/IIB	13/IIIB	14/IVB	15/VB	16/VIB	17/VIIB	18/VIII
1 1.00794 1,-1 20.28 13.81 0.0899† **H** $1s^1$ Hydrogen																	2 4.00260 4.216 0.95 at 26 atm 0.1785† **He** $1s^2$ Helium
3 (6.941) 1 1615 453.7 0.534 **Li** [He]$2s^1$ Lithium	4 9.012182 2 2744 1560 1.85 **Be** [He]$2s^2$ Beryllium											5 10.811 3 4275 2348 2.37 **B** [He]$2s^2 2p^1$ Boron	6 12.0107 ±4,2 4675* 3915* 2.26 **C** [He]$2s^2 2p^2$ Carbon	7 14.0067 ±3,5,4,2 77.344 63.15 1.251† **N** [He]$2s^2 2p^3$ Nitrogen	8 15.9994 -2,-1 90.2 54.4 1.429† **O** [He]$2s^2 2p^4$ Oxygen	9 18.99840 -1 85.0 53.55 1.696† **F** [He]$2s^2 2p^5$ Fluorine	10 20.1797 27.07 24.56 0.900† **Ne** [He]$2s^2 2p^6$ Neon
11 22.989770 1 1156.1 371.0 0.971 **Na** [Ne]$3s^1$ Sodium	12 24.3050 2 1363 923 1.74 **Mg** [Ne]$3s^2$ Magnesium											13 26.981538 3 2792 933.5 2.6989 **Al** [Ne]$3s^2 3p^1$ Aluminum	14 28.0855 4,2 3538 1687 2.33 **Si** [Ne]$3s^2 3p^2$ Silicon	15 30.97376 ±3,5,4 553 317.3 1.82 **P** [Ne]$3s^2 3p^3$ Phosphorus	16 32.065 6,±2,4, 717.75 388.36 2.07 **S** [Ne]$3s^2 3p^4$ Sulfur	17 35.453 ±1,7,5,3 239.11 171.65 3.214† **Cl** [Ne]$3s^2 3p^5$ Chlorine	18 39.948 87.8 83.8 1.784† **Ar** [Ne]$3s^2 3p^6$ Argon
19 39.0983 1 1033 336.8 0.862 **K** [Ar]$4s^1$ Potassium	20 40.078 2 1757 1115 1.55 **Ca** [Ar]$4s^2$ Calcium	21 44.95591 3 3109 1814 2.99 **Sc** [Ar]$3d^1 4s^2$ Scandium	22 47.867 4,3,2 3560 1941 4.54 **Ti** [Ar]$3d^2 4s^2$ Titanium	23 50.9415 5,4,3,2 3680 2183 6.11 **V** [Ar]$3d^3 4s^2$ Vanadium	24 51.996 3,6,2 2945 2180 7.19 **Cr** [Ar]$3d^5 4s^1$ Chromium	25 54.9380 2,3,4,6,7 2234 1519 7.44 **Mn** [Ar]$3d^5 4s^2$ Manganese	26 55.845 3,2,6 3134 1811 7.874 **Fe** [Ar]$3d^6 4s^2$ Iron	27 58.9332 2,3 3200 1768 8.90 **Co** [Ar]$3d^7 4s^2$ Cobalt	28 58.6934 2,3 3186 1728 8.90 **Ni** [Ar]$3d^8 4s^2$ Nickel	29 63.546 2,1 2835 1357.8 8.96 **Cu** [Ar]$3d^{10} 4s^1$ Copper	30 65.409 2 1180 692.68 7.13 **Zn** [Ar]$3d^{10} 4s^2$ Zinc	31 69.723 1,3 2477 302.91 6.095 **Ga** [Ar]$3d^{10} 4s^2 4p^1$ Gallium	32 72.64 4 3106 1211.4 5.32 **Ge** [Ar]$3d^{10} 4s^2 4p^2$ Germanium	33 74.9216 ±3,5 876 (sub.) 1090 (28 atm.) 5.73 **As** [Ar]$3d^{10} 4s^2 4p^3$ Arsenic	34 78.96 4,6,-2 958 494 4.79 **Se** [Ar]$3d^{10} 4s^2 4p^4$ Selenium	35 79.904 ±1,7,5,3 331.95 265.95 3.12 **Br** [Ar]$3d^{10} 4s^2 4p^5$ Bromine	36 83.80 0,2 119.93 115.8 3.73† **Kr** [Ar]$3d^{10} 4s^2 4p^6$ Krypton
37 85.4678 1 961 312.46 1.532 **Rb** [Kr]$5s^1$ Rubidium	38 87.62 2 1655 1050 2.54 **Sr** [Kr]$5s^2$ Strontium	39 88.9059 3 3618 1795 4.47 **Y** [Kr]$4d^1 5s^2$ Yttrium	40 91.224 4 4682 2128 6.51 **Zr** [Kr]$4d^2 5s^2$ Zirconium	41 92.90638 5,3,4 5017 2730 8.57 **Nb** [Kr]$4d^4 5s^1$ Niobium	42 95.94 6,5,4,3,2 4912 2896 10.22 **Mo** [Kr]$4d^5 5s^1$ Molybdenum	43 (98) 7,5,4 4538 2430 11.5* **Tc** [Kr]$4d^5 5s^2$ Technetium	44 101.07 2,3,4,6,8 4423 2607 12.37 **Ru** [Kr]$4d^7 5s^1$ Ruthenium	45 102.90550 2,3,4 3968 2237 12.41 **Rh** [Kr]$4d^8 5s^1$ Rhodium	46 106.42 2,4 3236 1828 12.0 **Pd** [Kr]$4d^{10}$ Palladium	47 107.8682 1 2435 1234.93 10.50 **Ag** [Kr]$4d^{10} 5s^1$ Silver	48 112.41 2 1040 594.22 8.65 **Cd** [Kr]$4d^{10} 5s^2$ Cadmium	49 114.82 3 2345 429.75 7.31 **In** [Kr]$4d^{10} 5s^2 5p^1$ Indium	50 118.710 4,2 2875 505.08 7.31 **Sn** [Kr]$4d^{10} 5s^2 5p^2$ Tin	51 121.760 ±3,5 1860 903.78 6.69 **Sb** [Kr]$4d^{10} 5s^2 5p^3$ Antimony	52 127.60 4,6,-2 1261 722.66 6.24 **Te** [Kr]$4d^{10} 5s^2 5p^4$ Tellurium	53 126.90447 ±1,5,7 457.51 386.85 4.93 **I** [Kr]$4d^{10} 5s^2 5p^5$ Iodine	54 131.29 0,2,4,6,8 165.11 161.4 5.90† **Xe** [Kr]$4d^{10} 5s^2 5p^6$ Xenon
55 132.90545 1 944 301.54 1.87 **Cs** [Xe]$6s^1$ Cesium	56 137.327 2 2170 1000 3.5 **Ba** [Xe]$6s^2$ Barium	57 138.9055 3 ★ 3737 1191 6.15 **La** [Xe]$5d^1 6s^2$ Lanthanum	72 178.49 4 4876 2506 13.31 **Hf** [Xe]$4f^{14} 5d^2 6s^2$ Hafnium	73 180.9479 5,4 5730 3290 16.65 **Ta** [Xe]$4f^{14} 5d^3 6s^2$ Tantalum	74 183.84 6,5,4,3,2 5828 3695 19.3 **W** [Xe]$4f^{14} 5d^4 6s^2$ Tungsten	75 186.207 7,6,5,4,3,2 5870 3459 21.0 **Re** [Xe]$4f^{14} 5d^5 6s^2$ Rhenium	76 190.23 4,8,6,3,2 5285 3306 22.57 **Os** [Xe]$4f^{14} 5d^6 6s^2$ Osmium	77 192.217 4,2,6,3 4700 2720 22.42 **Ir** [Xe]$4f^{14} 5d^7 6s^2$ Iridium	78 195.08 4,2 4098 2041.55 21.45 **Pt** [Xe]$4f^{14} 5d^9 6s^1$ Platinum	79 196.96655 3,1 3130 1337.33 19.3 **Au** [Xe]$4f^{14} 5d^{10} 6s^1$ Gold	80 200.59 2,1 629.88 234.32 13.55 **Hg** [Xe]$4f^{14} 5d^{10} 6s^2$ Mercury	81 204.3833 3,1 1746 577 11.85 **Tl** [Xe]$4f^{14} 5d^{10} 6s^2 6p^1$ Thallium	82 207.2 2,4 2022 600.61 11.35 **Pb** [Xe]$4f^{14} 5d^{10} 6s^2 6p^2$ Lead	83 208.9804 3,5 1837 544.55 9.75 **Bi** [Xe]$4f^{14} 5d^{10} 6s^2 6p^3$ Bismuth	84 (209) 4,2,6 — 527 9.3 **Po** [Xe]$4f^{14} 5d^{10} 6s^2 6p^4$ Polonium	85 (210) ±1,7,5,3 610* 575 — **At** [Xe]$4f^{14} 5d^{10} 6s^2 6p^5$ Astatine	86 (222) 0,2 211.4 202 9.73† **Rn** [Xe]$4f^{14} 5d^{10} 6s^2 6p^6$ Radon
87 (223) 1 950* 300 — **Fr** [Rn]$7s^1$ Francium	88 (226) 2 1413 973 5.0 **Ra** [Rn]$7s^2$ Radium	89 (227) 3 ★★ 3470* 1324 10.07 **Ac** [Rn]$6d^1 7s^2$ Actinium	104 (261) — — — **Rf** [Rn]$5f^{14} 6d^2 7s^{2*}$ Rutherfordium	105 (262) — — — **Db** [Rn]$5f^{14} 6d^3 7s^{2*}$ Dubnium	106 (266) — — — **Sg** [Rn]$5f^{14} 6d^4 7s^{2*}$ Seaborgium	107 (264) — — — **Bh** [Rn]$5f^{14} 6d^5 7s^{2*}$ Bohrium	108 (277) — — — **Hs** [Rn]$5f^{14} 6d^6 7s^{2*}$ Hassium	109 (268) — — — **Mt** [Rn]$5f^{14} 6d^7 7s^{2*}$ Meitnerium	110 (269) — — — **Ds** [Rn]$5f^{14} 6d^8 7s^{2*}$ (Darmstadtium)	111 (272) — — — **Uuu** [Rn]$5f^{14} 6d^9 7s^{2*}$ (Unununium)	112 (285) — — — **Uub** [Rn]$5f^{14} 6d^{10} 7s^{2*}$ (Ununbium)	113 (284) — — — **Uut** [Rn]$5f^{14} 6d^{10} 7s^2 7p^{1*}$ (Ununtrium)	114 (289) — — — **Uuq** [Rn]$5f^{14} 6d^{10} 7s^2 7p^{2*}$ (Ununquadium)	115 (288) — — — **Uup** [Rn]$5f^{14} 6d^{10} 7s^2 7p^{3*}$ (Ununpentium)	116 — — — **Uuh** [Rn]$5f^{14} 6d^{10} 7s^2 7p^4$ (Ununhexium)	117 **Uus** (Ununseptium)	118 **Uuo** (Ununoctium)

* Estimated Values

★	58 140.116 3,4 3716 1071 6.77 **Ce** [Xe]$4f^1 5d^1 6s^2$ Cerium	59 140.90765 3,4 3785 1204 6.77 **Pr** [Xe]$4f^3 6s^2$ Praseodymium	60 144.24 3 3347 1294 7.01 **Nd** [Xe]$4f^4 6s^2$ Neodymium	61 (145) 3 3273 1315 7.26 **Pm** [Xe]$4f^5 6s^2$ Promethium	62 150.36 3,2 2067 1347 7.52 **Sm** [Xe]$4f^6 6s^2$ Samarium	63 151.964 3,2 1869 1095 5.24 **Eu** [Xe]$4f^7 6s^2$ Europium	64 157.25 3 3546 1586 7.90 **Gd** [Xe]$4f^7 5d^1 6s^2$ Gadolinium	65 158.92534 3,4 3503 1629 8.23 **Tb** [Xe]$4f^9 6s^2$ Terbium	66 162.50 3 2840 1685 8.55 **Dy** [Xe]$4f^{10} 6s^2$ Dysprosium	67 164.9303 3 2973 1747 8.795 **Ho** [Xe]$4f^{11} 6s^2$ Holmium	68 167.26 3 3140 1802 9.07 **Er** [Xe]$4f^{12} 6s^2$ Erbium	69 168.9342 3,2 2223 1818 9.32 **Tm** [Xe]$4f^{13} 6s^2$ Thulium	70 173.04 3,2 1469 1092 6.903 **Yb** [Xe]$4f^{14} 6s^2$ Ytterbium	71 174.967 3 3675 1936 9.841 **Lu** [Xe]$4f^{14} 5d^1 6s^2$ Lutetium
★★	90 232.0381 4 5061 2023 11.72 **Th** [Rn]$6d^2 7s^2$ Thorium	91 231.0359 5,4 4300* 1845 15.4* **Pa** [Rn]$5f^2 6d^1 7s^2$ Protactinium	92 238.0289 6,5,4,3,2 4404 1408 18.95 **U** [Rn]$5f^3 6d^1 7s^2$ Uranium	93 (237) 5,6,4,3 4175* 917 20.2 **Np** [Rn]$5f^4 6d^1 7s^2$ Neptunium	94 (244) 4,6,5,3 3505 913 19.84 **Pu** [Rn]$5f^6 7s^2$ Plutonium	95 (243) 3,6,5,4,2 2284 1449 13.7 **Am** [Rn]$5f^7 7s^2$ Americium	96 (247) 3 — 1620 13.5* **Cm** [Rn]$5f^7 6d^1 7s^2$ Curium	97 (247) 2,3,4 — — 14* **Bk** [Rn]$5f^9 7s^2$ Berkelium	98 (251) 2,3,4 — 1170* — **Cf** [Rn]$5f^{10} 7s^2$ Californium	99 (252) 3 — 1130* — **Es** [Rn]$5f^{11} 7s^2$ Einsteinium	100 (257) 3 — 1800* — **Fm** [Rn]$5f^{12} 7s^2$ Fermium	101 (258) 3 — 1100* — **Md** [Rn]$5f^{13} 7s^2$ Mendelevium	102 (259) 2,3 — 1100* — **No** [Rn]$5f^{14} 7s^2$ Nobelium	103 (262) 3 — 1900* — **Lr** [Rn]$5f^{14} 6d^1 7s^2$ Lawrencium



NOTES:

(1) Black — solid.
Red — gas.
Blue — liquid.
Outline — synthetically prepared.

(2) Based upon carbon-12. ( ) indicates most stable or best known isotope.

(3) Entries marked with daggers refer to the gaseous state at 273 K and 1 atm and are

The A & B subgroup designations, are those recommended by the International Union of Pure and Applied Chemistry.

Sargent-Welch
VWR

TABLE OF PERIODIC PROPERTIES OF THE ELEMENTS

Percent Ionic Character of a Single Chemical Bond

Difference in electronegativity	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0	2.1	2.2	2.3	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2
Percent ionic character %	0.5	1	2	4	6	9	12	15	19	22	26	30	34	39	43	47	51	55	59	63	67	70	74	76	79	82	84	86	88	89	91	92

DATA CONCERNING THE MORE STABLE ELEMENTARY (SUBATOMIC) PARTICLES

	Neutron	Proton	Electron*	Neutrino*	Photon
Symbol	n	P	e (e-)	ν	γ
Rest mass (kg)	1.67495×10^{-27}	1.67265×10^{-27}	9.1095×10^{-31}	~0	0
Relative atomic mass ($^{12}C=12$)	1.008665	1.007276	5.48580×10^{-4}	~0	0
Charge (C)	0	1.60219×10^{-19}	-1.60219×10^{-19}	0	0
Radius (m)	8×10^{-16}	8×10^{-16}	$<1\times10^{-16}$	~0	0
Spin quantum number	1/2	1/2	1/2	1/2	1
Magnetic Moment†	$-1.913\ \mu_N$	$2.793\ \mu_N$	$1.001\ \mu_B$	0	0

* The positron (e+) has properties similar to those of the (negative) electron or beta particle except that its charge has opposite sign (+). The antineutrino ($\bar{\nu}$) has properties similar to those of the neutrino except that its spin (or rotation) is opposite in relation to its direction of propagation.

An antineutrino accompanies release of an electron in radioactive β (particle) decay, whereas a neutrino accompanies the release of a positron in β^+ decay.

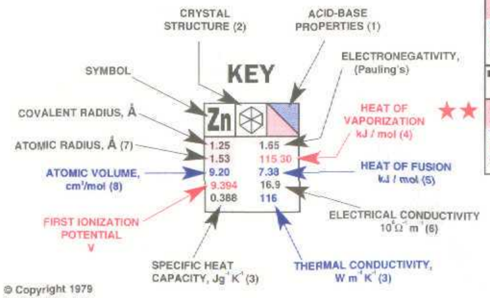
† μ_B=Bohr magneton and μ_N=Nuclear magneton.

GROUP 1/IA · 2/IIA · 3/IIIA · 4/IVA · 5/VA · 6/VIA · 7/VIIA · 8 · 9 VIIIA · 10 · 11/IB · 12/IIB · 13/IIIB · 14/IVB · 15/VB · 16/VIB · 17/VIIB · 18/VIII

Symbol	Covalent radius, Å	Atomic radius, Å (7)	Atomic volume, cm³/mol (8)	First ionization potential V	Specific heat capacity, Jg⁻¹K⁻¹ (3)	Electronegativity (Pauling's)	Heat of vaporization kJ/mol (4)	Heat of fusion kJ/mol (5)	Electrical conductivity 10⁶Ω⁻¹m⁻¹ (6)	Thermal conductivity, W m⁻¹K⁻¹ (3)
H	0.32	0.79	14.10	13.598	14.304	2.20	0.4581	0.0585	—	0.1815
He	0.93	0.49	31.80	24.587	5.193	—	0.084	0.021	—	0.152
Li	1.23	2.05	13.10	5.392	3.582	0.98	147.1	3.0	11.7	84.7
Be	0.90	1.40	5.0	9.323	1.825	1.57	297	11.71	25	200
B	0.82	1.17	4.6	8.298	1.026	2.04	507.6	22.6	5×10^{-12}	27.0
C	0.77	0.91	5.30	11.260	0.709	2.55	715	—	0.07	80-230
N	0.75	0.75	17.30	14.534	1.042	3.04	2.793	0.36	—	0.02598
O	0.73	0.65	14.0	13.618	0.918	3.44	3.410	0.222	—	0.2674
F	0.72	0.57	17.10	17.422	0.824	3.98	3.27	0.26	—	0.0279
Ne	0.71	0.51	16.90	21.564	1.030	—	1.77	0.34	—	0.0493
Na	1.54	2.23	23.70	5.139	1.228	0.93	98.01	2.601	20.1	141
Mg	1.36	1.72	14.0	7.646	1.02	1.31	127.6	8.95	22.4	156
Al	1.18	1.82	10.0	5.986	0.90	1.61	290.8	10.7	37.7	237
Si	1.11	1.46	12.1	8.152	0.70	1.90	359.0	50.2	4×10^{-4}	148.
P	1.06	1.23	17.0	10.487	0.769	2.19	12.4	0.63	10^{-15}	0.235
S	1.02	1.09	15.50	10.360	0.710	2.58	10	1.73	5×10^{-16}	0.269
Cl	0.99	0.97	18.70	12.967	0.479	3.16	10.20	3.21	—	0.0089
Ar	0.98	0.88	24.20	15.759	0.520	—	6.506	1.188	—	0.0177
K	2.03	2.77	45.30	4.341	0.757	0.82	76.9	2.33	16.4	102.5
Ca	1.74	2.23	29.90	6.113	0.647	1.00	154.67	8.53	31.3	200
Sc	1.44	2.09	15.0	6.56	0.568	1.36	304.80	16.11	1.5	15.8
Ti	1.32	2.00	10.60	6.83	0.523	1.54	425.2	18.6	2.6	21.9
V	1.22	1.92	8.35	6.75	0.489	1.63	446.7	22.8	4.0	30.7
Cr	1.18	1.85	7.23	6.766	0.449	1.66	339.5	20	7.9	93.7
Mn	1.17	1.79	7.39	7.434	0.479	1.55	219.74	14.64	0.5	7.82
Fe	1.17	1.72	7.1	7.902	0.449	1.83	349.5	13.8	11.2	80.2
Co	1.16	1.67	6.70	7.86	0.421	1.88	373.3	16.2	17.9	100
Ni	1.15	1.62	6.60	7.640	0.444	1.91	377.5	17.2	14.6	90.7
Cu	1.17	1.57	7.1	7.726	0.385	1.90	300.5	13.14	60.7	401
Zn	1.25	1.53	9.2	9.394	0.388	1.65	115.31	7.38	16.9	116
Ga	1.26	1.81	11.8	5.999	0.371	1.81	256.06	5.59	1.8	40.6
Ge	1.22	1.52	13.6	7.899	0.32	2.01	334.30	31.80	3×10^{-6}	59.9
As	1.20	1.33	13.1	9.79	0.29	2.18	32.4	27.7	3.8	50
Se	1.16	1.22	16.50	9.752	0.321	2.55	26.32	5.44	8	2.04
Br	1.14	1.12	23.5	11.814	0.226	2.96	14.725	5.285	10^{-16}	0.122
Kr	1.89	1.03	32.20	13.999	0.248	—	9.03	1.64	—	0.00949
Rb	2.16	2.98	55.9	4.177	0.363	0.82	69.2	2.34	47.8	58.2
Sr	1.91	2.45	33.7	5.695	0.301	0.95	136.9	8.2	5.0	35.3
Y	1.62	2.27	19.8	6.22	0.30	1.22	393.30	17.15	1.8	17.2
Zr	1.45	2.16	14.1	6.63	0.278	1.33	590.5	21	2.3	22.7
Nb	1.34	2.08	10.80	6.76	0.265	1.6	690.1	26.9	6.6	53.7
Mo	1.30	2.01	9.4	7.092	0.25	2.16	590.4	36	17.3	138
Tc	1.27	1.95	8.5	7.28	0.24	1.9	502	23	0.001	50.6
Ru	1.25	1.89	8.3	7.36	0.238	2.2	567.77	25.52	14.9	117
Rh	1.25	1.83	8.30	7.46	0.243	2.28	495.39	21.76	23	150
Pd	1.28	1.79	8.9	8.34	0.244	2.20	393.3	16.74	10.0	71.8
Ag	1.34	1.75	10.3	7.576	0.235	1.93	250.63	11.3	62.9	429
Cd	1.41	1.71	13.1	8.993	0.232	1.69	99.87	6.07	14.7	96.8
In	1.44	2.00	15.7	5.786	0.233	1.78	226.35	3.26	3.4	81.6
Sn	1.41	1.72	16.3	7.344	0.228	1.96	290.37	7.2	8.7	66.6
Sb	1.40	1.53	18.40	8.608	0.207	2.05	67.97	19.83	2.6	24.3
Te	1.36	1.42	20.5	9.009	0.202	2.1	50.63	17.49	2×10^{-4}	2.35
I	1.33	1.32	25.70	10.451	0.145	2.66	20.9	7.76	10^{-11}	0.449
Xe	1.31	1.24	42.90	12.130	0.158	2.6	12.64	2.30	—	0.00569
Cs	2.35	3.34	70	3.894	0.24	0.79	67.740	2.09	5.3	35.9
Ba	1.98	2.78	39.0	5.212	0.204	0.89	140.2	8.01	2.8	18.4
La★	1.25	2.74	22.50	5.58	0.195	1.10	399.57	11.30	1.9	13.5
Hf	1.44	2.16	13.60	6.825	0.144	1.3	661.07	21.76	3.4	23.0
Ta	1.34	2.09	10.90	7.55	0.140	1.5	737.0	36	8.1	57.5
W	1.30	2.02	9.53	7.864	0.132	2.36	422.58	35.4	18.2	174
Re	1.28	1.97	8.85	7.833	0.137	1.9	707.10	33.05	5.8	47.9
Os	1.26	1.92	8.43	8.438	0.130	2.2	627.6	29.29	12.3	87.6
Ir	1.27	1.87	8.54	8.967	0.131	2.20	563.58	26.36	21.3	147
Pt	1.30	1.83	9.10	8.959	0.13	2.28	510.45	19.66	9.4	71.6
Au	1.34	1.79	10.20	9.225	0.129	2.54	324.43	12.36	48.8	317
Hg	1.49	1.76	14.80	10.437	0.140	2.00	59.30	2.292	1.0	8.34
Tl	1.48	2.08	17.20	6.108	0.129	2.04	162.09	4.27	5.6	46.1
Pb	1.47	1.81	18.30	7.416	0.129	2.33	177.9	4.77	4.8	35.3
Bi	1.46	1.63	21.30	7.289	0.122	2.02	179	11.0	0.9	7.87
Po	1.53	1.53	22.70	8.41	—	2.0	120	13	0.7	20
At	1.47	1.43	—	—	—	2.2	30	12*	—	1.7
Rn	—	1.34	50.5	10.748	0.094	—	16.4	2.9	—	0.00364
Fr	—	2.7	—	4.073	—	0.7	64*	2.1*	—	15
Ra	—	—	45.2	5.278	0.094	0.9	136.82	8.37	1.0	18.6
Ac★★	—	—	22.5	5.17	0.120	1.1	—	—	—	12
Rf	—	—	—	—	—	—	—	—	—	—
Db	—	—	—	—	—	—	—	—	—	—
Sg	—	—	—	—	—	—	—	—	—	—
Bh	—	—	—	—	—	—	—	—	—	—
Hs	—	—	—	—	—	—	—	—	—	—
Mt	—	—	—	—	—	—	—	—	—	—
Ds	—	—	—	—	—	—	—	—	—	—
Uuu	—	—	—	—	—	—	—	—	—	—
Uub	—	—	—	—	—	—	—	—	—	—
Uut	—	—	—	—	—	—	—	—	—	—
Uuq	—	—	—	—	—	—	—	—	—	—
Uup	—	—	—	—	—	—	—	—	—	—
Uuh	—	—	—	—	—	—	—	—	—	—
★ Ce	1.65	2.70	21.0	5.538	0.19	1.12	313.80	9.20	1.4	11.4
Pr	1.65	2.67	20.80	5.473	0.193	1.13	332.63	10.04	1.5	12.5
Nd	1.64	2.64	20.6	5.525	0.190	1.14	283.68	10.88	1.6	16.5
Pm	1.63	2.62	22.4	5.582	—	1.13	—	—	2	17.9*
Sm	1.62	2.59	19.90	5.644	0.197	1.17	191.63	11.09	1.1	13.3
Eu	1.85	2.56	28.9	5.67	0.182	1.2	175.73	10.46	1.1	13.9
Gd	1.61	2.54	19.90	6.15	0.236	1.20	311.71	15.48	0.8	10.6
Tb	1.59	2.51	19.20	5.864	0.182	1.1	—	—	0.9	11.1
Dy	1.59	2.49	19.0	5.939	0.173	1.22	230	11.06	1.1	10.7
Ho	1.58	2.47	18.70	6.021	0.165	1.23	251.04	17.15	1.1	16.2
Er	1.57	2.45	18.40	6.108	0.168	1.24	292.88	17.15	1.2	14.3
Tm	1.56	2.42	18.10	6.184	0.160	1.25	191*	16.8*	1.3	16.8
Yb	1.70	2.40	24.80	6.254	0.155	1.1	128*	7.7*	3.7	34.9
Lu	1.56	2.25	17.80	5.426	0.154	1.27	355*	18.6*	1.5	16.4
★★ Th	1.65	—	19.90	6.31	0.113	1.3	543.92	15.65	7.1	54
Pa	—	—	15.0	5.89	—	1.5	—	—	5.6	47
U	1.42	—	12.50	6.194	0.12	1.38	422.58	15.48	3.6	27.6
Np	—	—	21.10	6.266	—	1.36	—	—	0.8	6.3
Pu	1.08	—	12.32	6.026	0.13*	1.28	—	—	0.7	6.74
Am	—	—	20.8	5.974	—	1.3*	—	—	0.7	10*
Cm	—	—	18.3	5.991	—	1.3*	—	—	—	10*
Bk	—	—	—	6.198	—	1.3*	—	—	—	10*
Cf	—	—	—	6.282	—	1.3*	—	—	—	10*
Es	—	—	—	6.42	—	1.3*	—	—	—	10*
Fm	—	—	—	6.5	—	1.3*	—	—	—	10*
Md	—	—	—	6.58	—	1.3*	—	—	—	10*
No	—	—	—	6.65	—	1.3*	—	—	—	10*
Lr	—	—	—	4.9*	—	1.3*	—	—	—	10*

*ESTIMATED VALUES

KEY



NOTES: (1) For representative oxides (higher valence) of group. Oxide is acidic if color is red, basic if color is blue and amphoteric if both colors are shown. Intensity of color indicates relative strength.

(2) Cubic, face centered; cubic, body centered; cubic; hexagonal; rhombohedral; tetragonal; orthorhombic; monoclinic.

(3) At 300 K (27°C)
(4) At boiling point
(5) At melting point
(6) Generally at 293 K (20°C) for polycrystalline material
(7) Quantum mechanical value for free atom
(8) From density at 300 K (27°C) for liquid and solid elements; values for gaseous elements refer to liquid state at boiling point

The A & B subgroup designations, are those recommended by the International Union of Pure and Applied Chemistry.

Sargent-Welch
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