1

Combustion of Energetic Materials

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Princeton-Combustion Institute
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Background in Energetic Materials Combustion

Penn State University

Research Laboratories

- Center for Combustion, Power, and Propulsion Laboratories (formerly PERC) – Combustion Research Laboratories @ Research East
- High Pressure Combustion Laboratory (Emeritus Prof. Ken Kuo)
- Cryogenic Combustion Laboratory (Emeritus Professor Bob Santoro)

Energetic Materials

Explosives

Propellants

Pyrotechnics

no oxidizer needed, temperature sensitive reactions, highly exothermic

Some Applications

- Blasting explosives for mining, tunneling, demolition, and weaponry
- Explosive bolts and actuators
- Propellants for rockets and guns
- Gas generators, for fire extinguishers or for air bag inflators (rapidly produce large amount of gas to inflate a nylon or polyester bag in some 50 ms - inflates at 100 m/s)
- Light generators (sparklers), for fireworks or for rescue signals, including underwater signals: produce bright light (yellow-white by hot emission at > 1500 K) and colored shimmering sparks
- Smoke generators, for rescue signals or military purpose (smoke grenades)
- Noise generators for fireworks, for rescue signals, stun-grenades
- Combustion synthesis
- Microthrusters, microactuators, micropyrotechnics
- Chemical storage for hydrogen
- Emergency airplane crew and passenger escape systems

Some history of energetic materials

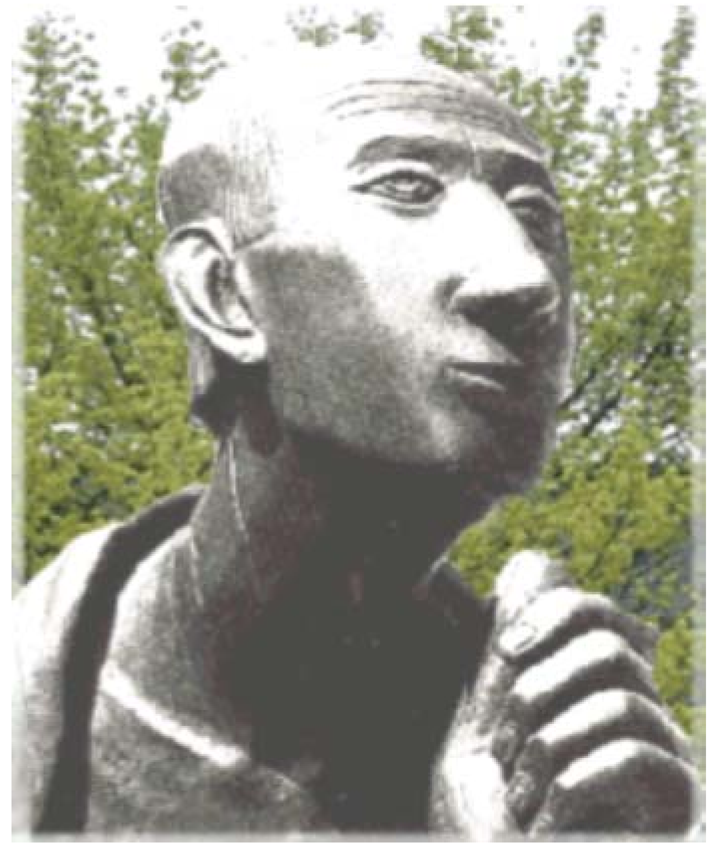
- Black powder was the discovery, at the end of the first millennium, of Chinese alchemists who may have been experimenting with various flame-producing materials
- Their studies involved the mixing and heating of various substances including sulfur, charcoal, and eventually saltpeter (potassium nitrate)
- Depending upon the proportions of ingredients, explosive or propelling properties were achieved, which were applied to various pyrotechnic devices, including fireworks and rockets, called fire arrows
- From China, knowledge spread to India, to the Arab countries and finally Europe

Roger Bacon

- Roger Bacon (1214-1292) brought the knowledge of black powder to Europe
- Kept the secret to himself

Albertus Magnus

- St. Albert the Great (ca. 1200-1280)
- Spread knowledge of black powder across Europe



Paul Vieille

- There had been experiments on new powder formulations since the beginning of the 19th century without much success and with big accidents
- However, the elimination of smoke and solid residues was necessary for many practical applications
- First breakthrough in making a smokeless powder came in France in 1886
- Paul Vieille found ways to nitrate cotton so that it was possible to dissolve in solvents, which led to gelatinized masses of nitrocellulose, which could be formed into grains

Alfred Noble

- Family business was production of nitroglycerine
- Factory destroyed in 1864
- Developed fulminate detonator
- Developed dynamite and blasting gelatine
- In 1887, Nobel patented Ballistite, based on nitrocellulose plasticized by nitroglycerine
- It was the first step in the direction of an extruded double-base (EDB) energetic material

John W. Parsons

- Composite propellants are the base of all modern developments of solid rocket propulsion systems
- In 1942, John W. Parsons invented the first cast composite propellant
- While watching tar paper being applied to the roof of a building, he realized that asphalt mixed with the right solid oxidizer could make a good propellant
- Easily poured and formed when hot, it would cool and dry without brittleness and cracking that plagued the use of black powder mixtures

Power Densities

- Acetylene/air flame – 10^2 W/cm^3
- Deflagration of an energetic material (e.g., a gun propellant) – 10^6 W/cm^3
- Detonating high explosive 10^{10} W/cm^3

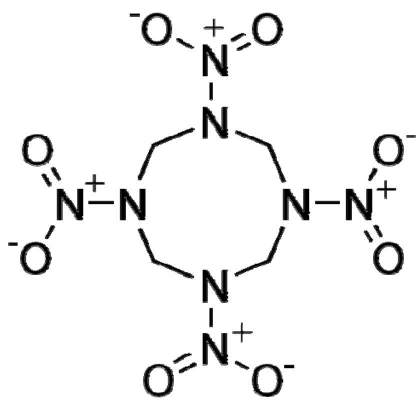
Energy

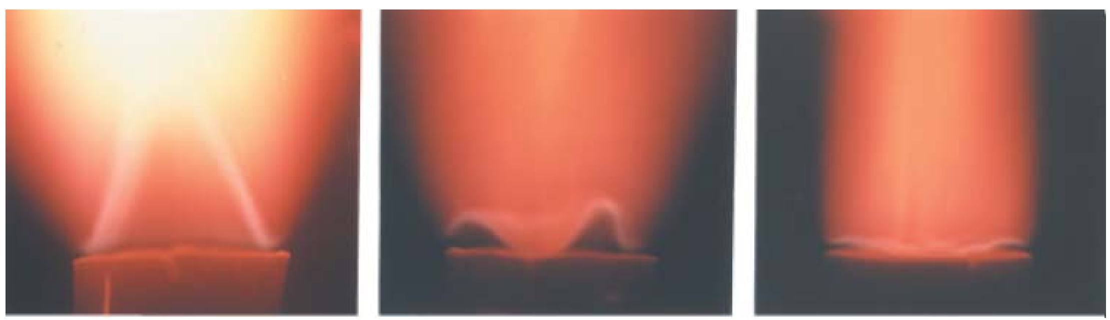
Thermodynamic energy densities of monomolecular and composite systems

	High energy
ADN/Al max.	23 kJ/cc
Compression moldable	19-22
Strategic propellants	14-16
CL-20 (neat)	12.6
Tritonal	12.1
HMX (neat)	11.1
LX-14	10.0
TATB (neat)	8.5
Comp. C-4 as used	8.0
LX-17	7.7
TNT (neat)	7.6
	Low energy

Monomolecular EMs have oxygen and fuel on same molecule

- HMX



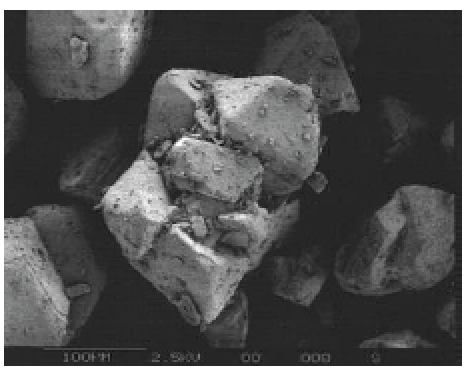


Deflagrating at increasing pressures

Detonating

What are plastic bonded explosives?

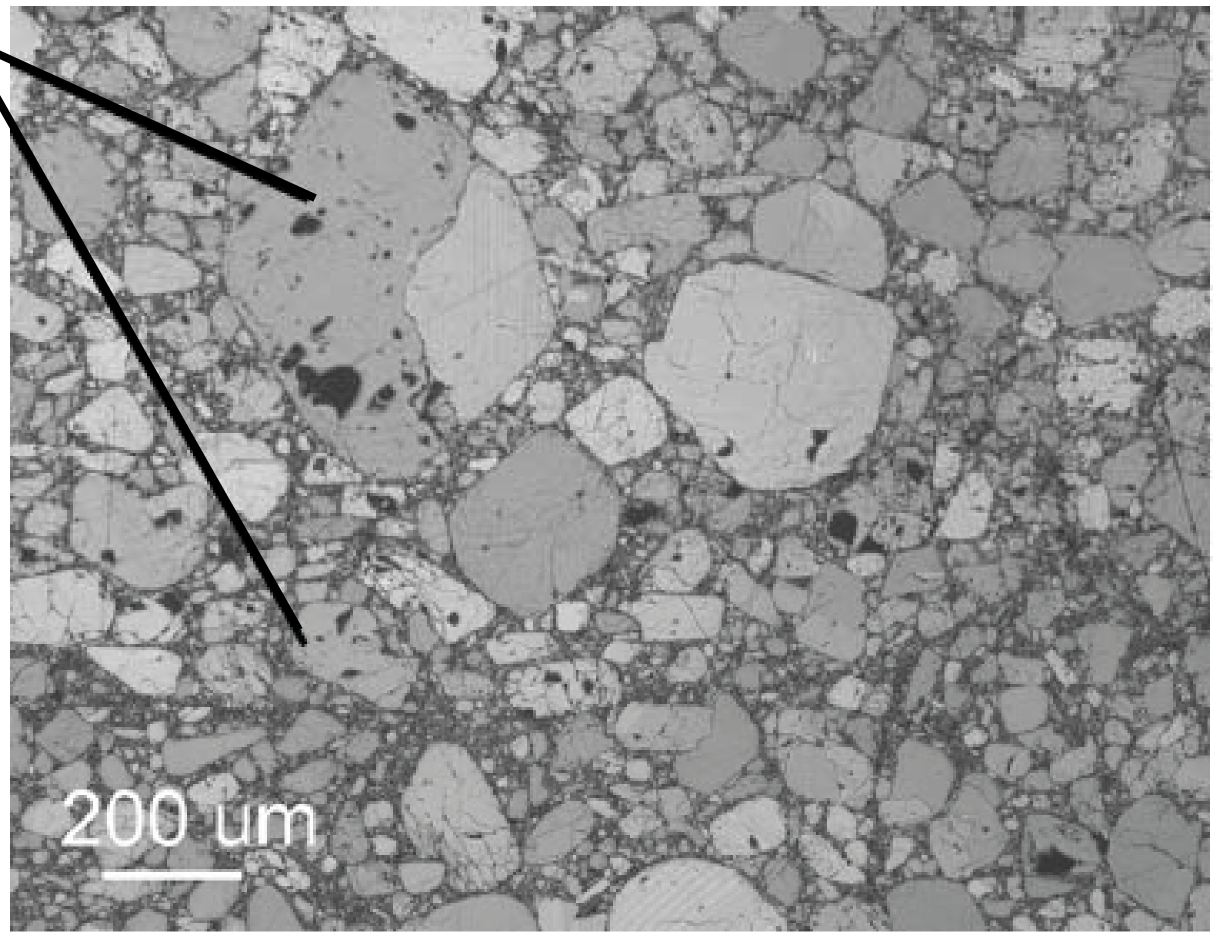
- Developed based on similar chemical processes as those used to develop composite rocket propellants – crystalline materials such as HMX and RDX are mixed with liquid copolymers such as polystyrene and polybutadiene prepolymers, then crossed linked and cured.
- 95% HMX + 2.5% estane + 2.5% BDNPA/F equals PBX9501



Photomicrograph of a pressed plastic bonded explosive

PBX 9501

HMX grains



Propellants

Liquid

Monopropellants

Examples: Nitromethane, hydrazine, aqueous HAN (hydroxylammonium nitrate)

Bipropellants (multicomponent)

Examples: LH2/LOX

Hybrid

Examples: HTPB/LOX

Solid

Homogeneous

Examples (NC – single base, NC/NG – double base, NC/NG/RDX – triple base)

Composite

Examples AP/HTPB, AP/HTPB/Al, RDX/HTPB/AP/Al

Pyrotechnics

- Fireworks of various kinds, thermite (redox, e.g., $Al+Fe_2O_3$), intermetallic (e.g., Al + Ni), igniters, incendiaries
- Pyrotechnics often used in the international community the same as the usage of energetic materials (EMs)

Thermite example

Definition of Solid Propellants

- A solid propellant is a solid state substance which contains both oxidizer and fuel and is able to burn in absence of ambient air
- Solid propellants usually generate a large number of gaseous molecules at high temperatures (T_f = 2,300-3,800 K) during combustion. Condensed phase species are produced, especially from metalized solid propellants.
- High-temperature combustion products are mainly used for propulsion and gas generation purposes
- There are two types of solid propellants that are differentiated by the condition in which their ingredients are connected:
  - Homogeneous: the oxidizer and fuel are chemically linked and form a single chemical structure. These propellants are physically homogeneous.
  - Heterogeneous: the oxidizer and fuel are physically mixed but do not have chemical bonds between them. These propellants are physically heterogeneous.

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Desirable Characteristics of Solid Propellants

- High gas temperature and/or low molecular mass
- High density
- Good mechanical and bond properties
- Good aging characteristics
- Desirable ignition characteristics
- Low-hazard manufacturing and handling
- Predictable and reproducible properties
- Low thermal expansion coefficient
- Low temperature sensitivity
- Non-toxic exhaust gases with minimum smoke
- Low absorption of moisture
- Minimum sensitivity of burning velocity to pressure, temperature and gas velocity (erosive burning)

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Homogeneous Propellants

- Uniform physical structure
- Fuel and oxidizer are chemically bonded together
- Major constituents are nitrocellulose (NC) and nitroglycerine (NG)
- Nitrocellulose is a typical example of homogeneous propellants. Nitrocellulose is a nitrated cellulose whose chemical structure is represented by

  $C_6H_{7.55}O_5(NO_2)_{2.45}$ and $C_6H_{7.0006}N_{2.9994}O_{10.9987}$

  for 12.6% and 14.14% nitrogen content, respectively.
- Propellants which are composed of NC and NG are called double-base propellants and are typical homogeneous propellants

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Calculation of Oxygen Balance

- The oxygen balance is the amount of oxygen in weight percentage, which is liberated as a result of complete conversion of the energetic material into CO_2, H_2O, SO_2, Al_2O_3 etc. In this case, the oxygen balance is a positive percentage.

$$\text{Oxygen Balance} = \frac{\text{Mass of excess oxygen in 1 mole of compound}}{\text{Mass of 1 mole of compound}} \quad (1)$$

- If oxygen is needed for the complete combustion of the energetic material (EM) then the oxygen balance is a negative percentage
- The calculation of oxygen balance is performed by assuming the conversion of the atoms (C, H, N, O, and Al, etc.) into fully oxidized molecules:

$$C \rightarrow CO_2 \qquad N \rightarrow 0.5\, N_2 \qquad H \rightarrow 0.5\, H_2O \qquad Al \rightarrow 0.5\, Al_2O_3$$

  In case a compound contains Cl, consider $H + Cl \rightarrow HCl$ as the reaction.

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Oxygen Balance Example

- RDX ($C_3H_6O_6N_6$)

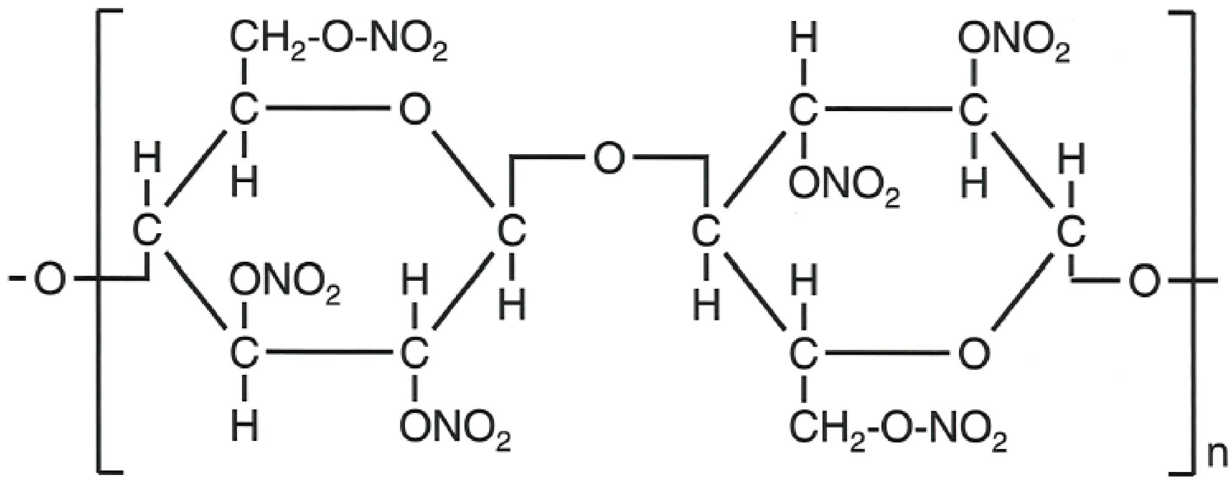
  $3C \rightarrow 3\ CO_2$, $6H \rightarrow 3\ H_2O$, $6N \rightarrow 3\ N_2$

- For complete combustion, 9 oxygen atoms are needed. The substance supplies 6 atoms, that means that 3 atoms are still required. The molecular weight of 3 g-atoms of oxygen is $3 \times 15.994 = 46.998$ g; and $46.998\ \text{g} \div 222.117\ \text{g} = 0.2161$.
- Therefore, the oxygen balance of RDX is

  -21.61%

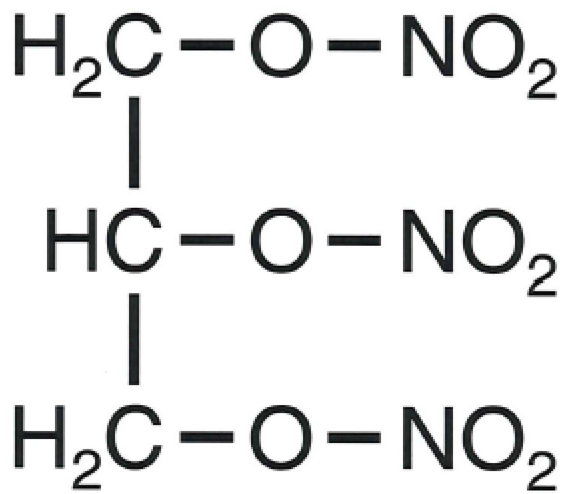
Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Molecular Structure and Thermochemical Properties of Nitrocellulose (NC)



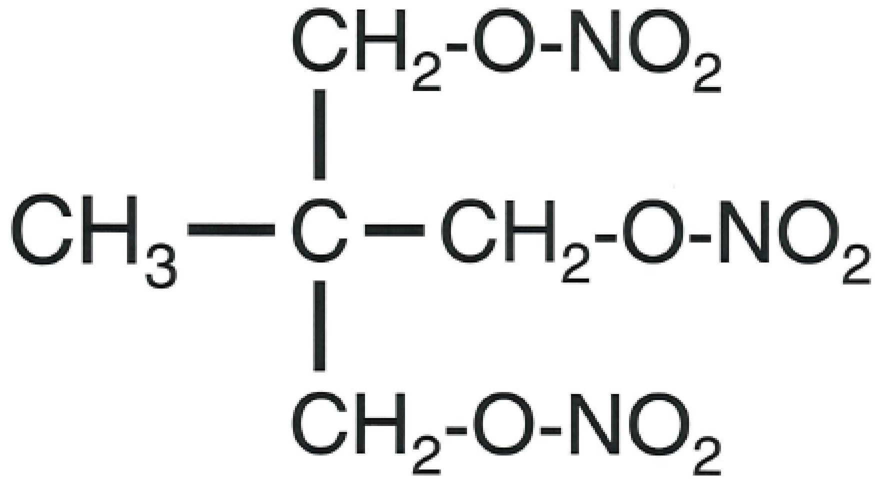
- Nitration level = 14.14%
- Molecular weight = 297.106 gm/mol
- Oxygen balance = -24.24%
- Density = 1.66 g/cc
- Heat of combustion = 650 kcal/mol
- Enthalpy of formation = -155.99 kcal/mol
- Physical state: solid

Molecular Structure and Thermochemical Properties of Nitroglycerine(NG)



- Molecular weight = 227.087 gm/mol
- Oxygen balance = 3.52%
- Density = 1.593 g/cc
- Heat of combustion = 364.3kcal/mol
- Enthalpy of formation = -84.90 to -118.90 kcal/mol
- Physical state: liquid

Molecular Structure and Thermochemical Properties of Trimethylolethane Trinitrate (TMETN)



- Molecular weight = 255.141 gm/mol
- Oxygen balance = -34.49%
- Density = 1.488 g/cc
- Heat of combustion = 674.0 kcal/mol
- Enthalpy of formation = -92.90 to -113.80 kcal/mol
- Physical state: liquid

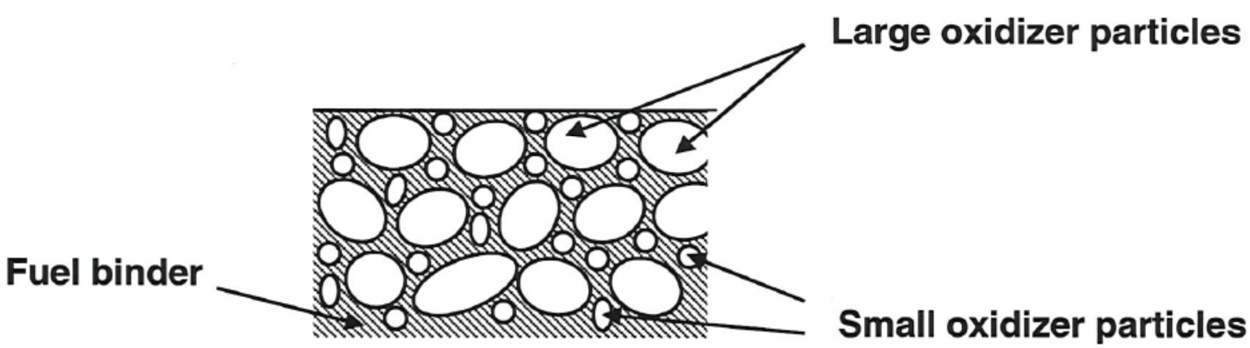
Some Decomposition Characteristics of NC

- When nitrocellulose is decomposed thermally, two major fragments are generated. One group of fragments with a C/H and C/H/O structure acts as a fuel with the other fragment of NO_2 acting as an oxidizer.
- Since nitrocellulose is a fibrous material, it is difficult to form a specified propellant grain using it as a single ingredient (called monopropellant)
- Liquid materials called "plasticizers" are usually mixed with the nitrocellulose to gelatinize it and to form a specific shape for the propellant grain
- Typical examples of plasticizers include nitroglycerin (NG) and trimethylolethane trinitrate (TMETN)
- Both of them (i.e., NG and TMETN) are also nitrated materials, which can individually function as propellants in the liquid form

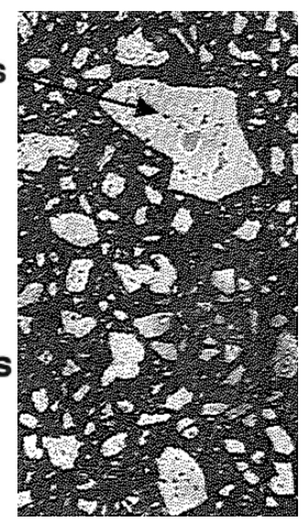
Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Heterogeneous (Composite) Propellants

- Non-uniform physical structure
- The fuel has a hydrocarbon structure such as hydroxyl-terminated polybutadiene (HTPB)
- The fuel has a dual function:
  - To produce energy when burned with oxidizer-rich species
  - To bind the oxidizer particles together to form a specified propellant grain shape
- The organic fuel material is initially in a liquid or semi-liquid form that can be cured to form a solid



Cross-sectional view of a composite propellant



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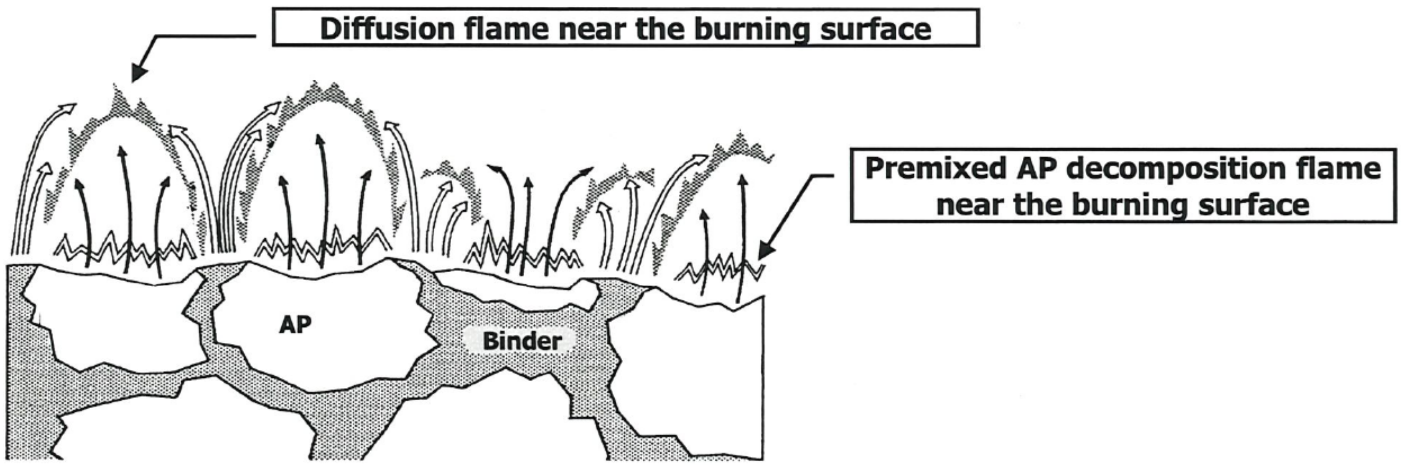
Heterogeneous (Composite) Propellants (cont’d)

- Composite propellants are usually made of a polymeric matrix, loaded with a solid powder oxidizer, and possibly a metal powder (e.g., aluminum) that plays the role of a secondary fuel component
- The oxidizer and fuel containing molecules come from separate components. Therefore, the flame structure is 3D and non-premixed



- The major propellant properties, such as burning rate, rheology, and mechanical behavior, are directly dependent on the size and distribution of fuel and oxidizer particles in the matrix
- Oxidizer and metallic fuel ingredients are in the form of solid powders, which must be mixed with a binder to provide cohesion and distribution

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Major types of Ingredients in Solid Propellants

- **Oxidizer**: usually crystalline particles to supply oxygen-rich species
- **Fuel binder**: liquid from hydrocarbon polymers holds the solid oxidizer particles together and provides fuel-rich component for burning. Also controls the Mechanical Properties.
- **Plasticizer**: for obtaining superior characteristics of grain formation, to improve mechanical properties, and to reduce shock sensitivities
- **Stabilizer**: for increasing chemical stability of composite solid propellants
- **Curing agent and/or Cross Linking agent**: for curing the prepolymers in the binder material and forming chemical bonds between the binder materials. Cross linking agent helps to form long chains and complex three-dimensional polymers.

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Major types of Ingredients in Solid Propellants

- **Bonding agent**: used to increase the adherence of each oxidizer particle to the binder
- **Burning rate catalyst**: for increasing the burning rate of solid propellants
- **Anti-aging agent**: used to avoid deterioration of the propellant physical properties with time
- **Opacifier**: used to make the propellant less translucent so that in-depth radiation absorption is avoided
- **Flame suppressant**: for suppressing the flame luminosity
- **Combustion instability suppressant**: for reducing the burning rate sensitivity to pressure fluctuations

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

List of Ingredients Used in Homogeneous Propellants

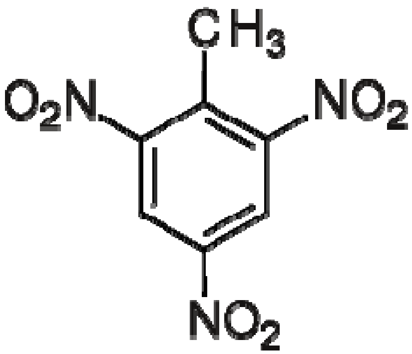
Type of Ingredient	Examples
Plasticizer (fuel and oxidizer)	NG: nitroglycerin TMETN: trimethylolethane nitrate TEGDN: triethylene dinitrate DEGDN: diethylene glycol dinitrate
Plasticizer (fuel)	DEP: diethylphtalate TA: triacetine PU:polyurethane
Binder (fuel and oxidizer)	NC: nitrocellulose
Stabilizer	EC: ethyl centralite 2NDPA: 2-nitrodiphenilamine
Burning rate catalyst	PbSa: lead salicylate PbSt: lead stearate CuSa: copper salicylate CuSt: copper stearate LiF: lithium fluoride
High energy additive	RDX: cyclotrimethylene trinitramine HMX: cyclotetrmethylene tetranitramine
Coolant	OXM: oxamide
Opacifier	C: carbon black
Flame suppressant	KNO3: potassium nitrate K2SO4: potassium sulfate
Metal fuel	Al: aluminum
Combustion instability suppressant	Al: aluminum, Zr: zirconium, ZrC: zirconium carbide

List of Ingredients Used in Heterogeneous Propellants

Type of Ingredient	Examples
Oxidizer	AP: ammonium perchlorate AN: ammonium nitrate NP: nitronium perchlorate KP: potassium perchlorate RDX: cyclotrimethylene trinitramine HMX: cyclotetramethylene tetranitramine
Binder	PBAN: polybutadiene acrylonitrile CTPB: carboxyl terminated polybutadiene HTPB: hydroxyl terminated polybutadiene
Curing and/or cross linking agents	PQD: peraquinone dioxime TDI: toluene-2,4-disocyanate MAPO: tris(1-(2-methyl) aziridinyl) phosphine oxide ERLA-0510: N,N,O-tri (1,2-epoxy propyl)-4-aminophenol IPDI: isophorone diisocyanate
Bonding Agent	MAPO: tris(1-(2-methyl) aziridinyl) phosphine oxide TEA: triethanolamine
Plasticizer	DOA: dioctyl adipate, IDP: isodecyl pelargonefe, DOP: dioctyl phthalate
Burning rate catalyst	Fe2O3: ferric oxide, FeO(OH): hydrated ferric oxide, nBF: n-butyl ferrocene, DnBF: di-n-butyl ferrocene
Metal fuel	Al: aluminum
Combustion instability suppressant	Al: aluminum, Zr: zirconium, ZrC: zirconium carbide

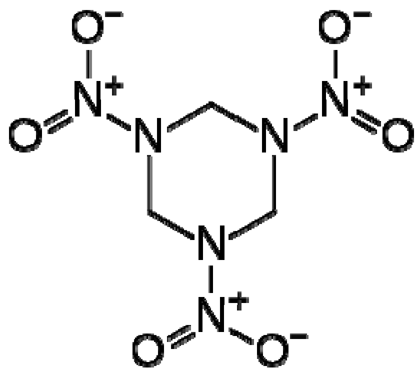
Molecular Structure of Some Explosive Ingredients

TNT



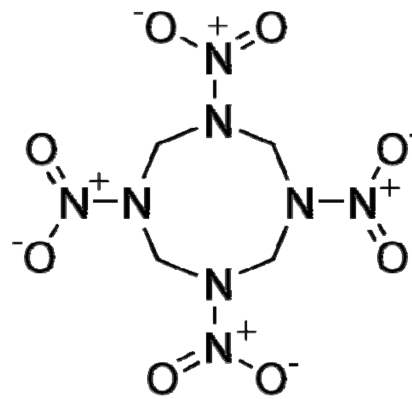
Trinitrotoluene

RDX



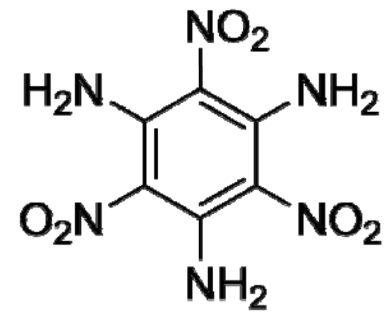
Cyclotrimethylene trinitramine

HMX



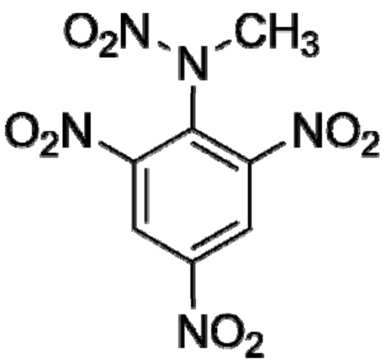
Cyclotetramethylene tetranitramine

TATB



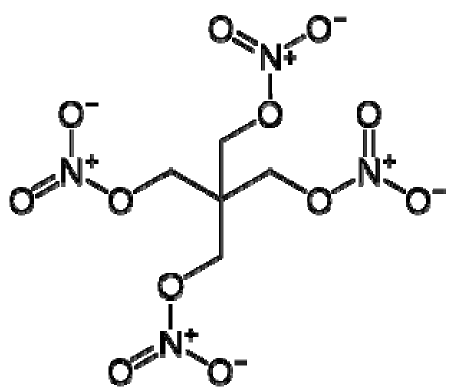
Triaminotrinitrobenzene

Tetryl



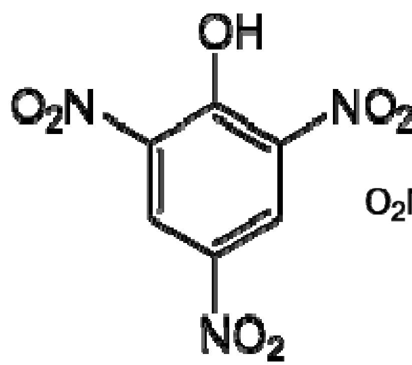
Trinitrophenyl methylnitramine

PETN



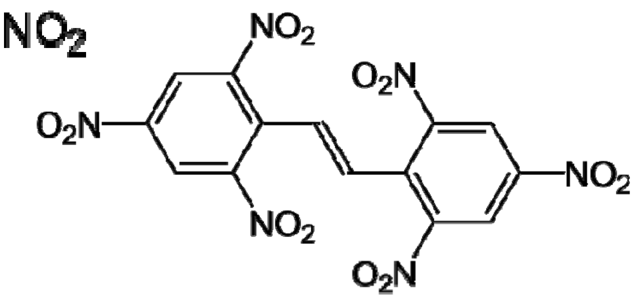
Pentaerythritoltetranitrate

Peric Acid



Trinitrophenol

HNS



Hexanitrostilbene

Properties of Several Solid Oxidizers

Oxidizer	Molecular Formula	Melting/ Decomposition Temperature (K)	ΔH_f^o (kJ/mol)	Density (kg/m^3)	Oxygen Balance %
AN	NH_4NO_3	443	-365.04	1720	20.0
AP	NH_4ClO_4	403	-296.00	1950	34.0
HP_2	$N_2H_6(ClO_4)_2$	443	-293.30	2200	41.0
HP	$N_2H_5ClO_4$	443	-177.80	1940	24.0
ADN	$NH_4N(NO_2)_2$	363	-150.60	1820	25.8
HNF	$N_2H_5C(NO_2)_3$	395	-72.00	1870-1930	13.1
NP	NO_2ClO_4	393	37.10	2220	66.0
RDX	$C_3H_6N_6O_6$	477	70.63	1820	-21.6
HMX	$C_4H_8N_8O_8$	548	74.88	1960	-21.6

HP_2 – hydrazine diperchlorate
HP – hydrazine perchlorate
NP – nitryl perchlorate
ADN – ammonium dinitramide
HNF – hydrazinium nitroformate

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Hazard Classification of Solid Propellants

The classification of the propellant (1.1 or 1.3) determines the *method of labeling* and the *cost of shipping* rocket propellants, loaded military missiles, explosives, or ammunition; it also determines the *limits on the amount of propellant stored or manufactured* in any one site and the *minimum separation distance* of that site to the next building or site.

Class 1.1

- Propellants that can experience a transition from deflagration to detonation are considered more hazardous and are usually designed as class 1.1-type propellants
- With a class 1.1 propellant, a powerful detonation can sometimes occur, which rapidly gasifies all the remaining propellant, and is much more powerful and destructive than the bursting of the rocket motor case under high pressures. Unfortunately, the term "explosion" has been used to describe both a bursting of the case with its fragmentation of the motor and also the higher rate of energy release of a detonation, which leads to a very rapid and more energetic fragmentation of the rocket motor.

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012

Hazard Classification of Solid Propellants *(cont.)*

<u>Class 1.3</u>

- Most propellants will burn, the rocket motor case may burst if chamber pressure becomes too high, but the propellant *will not detonate*
- If the rocket motor case should burst violently with a class 1.3 propellant, then much of the remaining unburnt propellant would be thrown out, but would eventually stop burning

Note:

Class 1.2 corresponds to non-mass detonating and fragment producing device

Class 1.4 corresponds to moderate fire, no detonation, and no fragment

Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012