Solid Rocket Motors

Solid Propellant Composition, Fabrication

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Solid Propellant Choice: Considerations

- **Energetics**
  - I_{sp} performance
- **Storage density**
  - motor size
- **Regression/burn rate characteristics**
  - operability/sensitivity (T, p, dynamics), burn area limits
- **Mechanical properties**
  - stiffness, modulus, thermal expansion,…
- **Vulnerability, hazards, emissions**
  - shock sensitivity, shipping, toxicity of products, smoke (observable)
- **Aging**
  - sag, temperature cycling, cracking, debonding, moisture, …
- **Manufacturability**
  - maximum web thickness and segment length, mixability, viscosity (complex grains), curing limits, …
- **Cost**

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

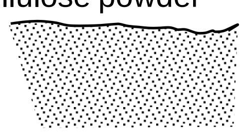
Solid Propellants Families

- Two basic types
- **Homogeneous**
  - reactants (fuel, oxidizer) mixed at molecular level
  - double-base propellants
    - used in early modern solid rockets
      - in US, initial work done by Navy and part of JPL
      - replaced gun/black powder,
      - used in WWII JATOs and early Sidewinders
- **Heterogeneous**
  - fuel and oxidizer are “macroscopically” separated
  - composite propellants

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Double-Base (DB) Propellants

- Generally main ingredients are
  - nitrocellulose NC (gun cotton, flash paper)
    - flammable powder (both “fuel and oxidizer”)
    - ~50-55% by mass
  - nitroglycerine NG
    - explosive liquid (both “fuel and oxid.”)
    - ~40-45% by mass
    - other liquid explosives also used (nitrates of glycol and other hydrocarbons)
- Liquid explosive absorbs into nitrocellulose powder
  - both ingredients can burn alone
  - molecular mixing of NC and NG



Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering

Other DB Ingredients

- Opacifier (<1%)
  - increase absorption of flame radiation (increase regression rate, reduce casing/insulator temperature)
  - carbon black, graphite
- Burn-rate modifier/catalysts (<few %)
  - increase regression rate
  - PbSa, CuSa (salicylates), PbSt, CuSt (stearates)
- Stabilizers (<few %)
  - enhance storage lifetime
  - ethyl centralite EC, diethyl diphenyl DED, …
- Flash suppressor (<2%)
  - reduce visible flame emission (e.g., tactical missiles)
  - potassium sulfate (K_2SO_4), potassium nitrate (KNO_3)

see Table 12-6 Sutton

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering

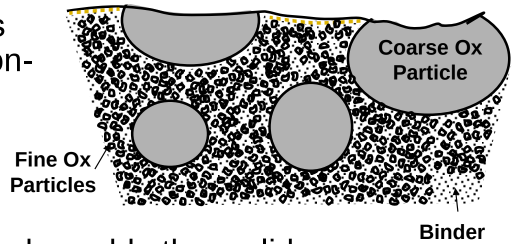
Manufacture of DB Propellants

- Extruded DB (EDB) propellants
  - produce desired shape by extruding through die
  - add lubricants
    - graphite, wax
    - ~0.3-1%
- Cast DB (CDB) propellants
  - cast shape by pouring mixture into pre-form mold/die with grain geometry then cure (chemical and thermal)
  - add plasticizers (organic liquids)
    - traicetin, diethyl phthalate, …
    - ~1-10%

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

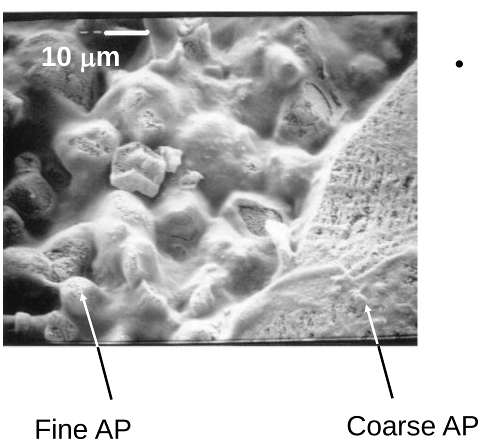
Composite Propellants (CP)

- "Oxidizer" particles held together in non-energetic polymer binder (fuel)
- Manufacture
  – grind oxidizer crystals into powder, add other solids (e.g., catalysts)
  – mix liquid binder with liquid curing agents, crosslinkers, plasticizers, stabilizers, bonding agents
  – mix solids and liquids, cast and cure



Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Cleaved Propellant Sample



- Scanning Electron Microscope (SEM) image
  – 92% solids (high level)
  – 10μm and 400μm AP oxidizer particles
  – HTPB binder

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

CP Ingredients – Oxidizers

	Name	Formula	Density (kg/m³)	Y_O (%)
AP	**ammonium perchlorate**	**NH_4ClO_4**	**1950**	**54.5**
AN	ammonium nitrate	NH_4NO_3	1730	60.0
KP	potassium perchlorate	$KClO_4$	2520	46.2
KN	potassium nitrate	KNO_3	2110	47.5
ADN	ammonium dinitramine	$NH_4N(NO_2)_2$	1800	51.6
SN	sodium nitrate	$NaNO_3$	2170	56.4

- Typically used inorganic oxidizers (normally 60-70%, <90% by mass)
  - perchlorates good oxidizers (AP most common) but HCl is product ⇒ forms acid with water AND ground water contamination issues
  - nitrates have generally lower performance (*r*); AN has low cost and produces no smoke; but AN phase (density) change if temp. cycled (debonding) and hydroscopic (degrades if abs. moisture)

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

CP Ingredients – Binders

	Name	Comments
PU	polyurethane	Polaris
PBAN	polybutadiene acrylonitrile	Titan/Shuttle SSRM
PNC	plasticized nitrocellulose	Minuteman/Polaris
CTPB	carboxy-terminated polybutadiene	Minuteman (Stg. 2,3)
HTPB	hydroxy-terminated polybutadiene	higher solids loading
GAP	glycidyl azide polymer (HC w/ O & N_3)	energetic binder
BAMO/ AMMO	bis-azidomethyloxetane/azideomethyl-methyloxetane	energetic binder

- Polymers to provide structural stability and fuel (<20%)
  - typically long-chain polymers, cross-linked during curing
  - must process well in mixing, casting, curing
  - must maintain integrity of propellant under loads, storage temperatures, stay bonded to particles
  - prefer "minimal" binder since "oxidizers" only partly O (also fuel,…)

most CP fuel-rich

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering

AP Example

- AP "oxidizer" can burn by itself at some pressures
- AP equilibrium composition at 1000 psi
  - T_o = 1400 K
  - χ_{H2O} = 38%
  - χ_{HCl} = 20%
  - χ_{N2} = 12%
  - χ_{O2} = 29%
- < 30% of AP available as "oxidizer" for binder

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering

CP Ingredients - Other

- Curing agents (< few %)
  - liquid added to promote cross-linking
  - IPDI, DDI, TMP, …
- Plasticizer (<5-7%)
  - liquid added to enhance casting process (lower viscosity, longer pot life before curing)
  - DOA, DOP, …
- Burn-rate modifiers/catalysts (<few %)
  - typically metal oxides: FeO, $CuCr_2O_4$, TiO_2, n-Butyl ferrocene, …
- Bonding agents, stabilizers, etc.

see Table 12-7 Sutton

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering

CP – Metallic Fuel Particles

	MW	Density (kg/m^3)	T_{ad}(K)*	Comments
Al	27	2700	5170	common, low cost, burns well
Be	9	2300	5820	most energetic, but toxic products
B	11	2400	4800	no smoke, poor comb. efficiency
Mg	24	1750	---	not energetic (T_o↓); no smoke – MgO(g)
Ti	48	4500	---	high density, low Isp
Zr	91	6400	---	high density, low Isp

*at 1000 psi with O_2

- Also add metal particles/powders (~2-21%)
  - increase propellant density (reduce vol., incr. τ)
  - can increase T_o (c^*, I_{sp})
  - for some metals, product is liquid (Al_2O_3, BeO)
    - smoke, agglomeration and slagging, can't expand in nozzle

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering

Manufacture of Composite Propellants

- Generally cast
  - pouring mixture into pre-form mold/die with grain geometry then cure (chemical and thermal)
  - propellant must be mixed with good uniformity, maintain wetting of solids, flow into mold easily, cure equally
    - high solids loading and small particles = high solid surface area ⇒ hard to mix and keep solids wetted

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering

High Energy Propellants

- For very high burn rate (tactical weapons)
- Use highly energetic organic oxidizers, explosives
  - crystalline nitramines
    - HMX, RDX
  - NC or NG
- Sensitive to impulse loading (e.g., detonate)
- May require modifiers to reduce press. expon. n
- RDX, HMX internally stoich. – when add binder usually add another oxidizer
  - minimum smoke: AN
  - reduced smoke: AP
  - smoky: AP+Al

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Georgia Tech College of Engineering

CP - DB Propellants

- To maintain “smokeless” or reduced smoke operation and modified performance can combine
  - Composite Modified Cast DB (CMDB) propellants
    - add HMX, RDX to casting powder in CDB
  - Elastomeric Modified Cast DB (EMCDB)
    - add hydroxyl prepolymer and cross-linking agent to modify propellant physical properties

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Case Bonded and Free Standing Grains

- **Case bonded grains**
  - propellant bonded to casing via liner, insulation
  - generally for >0.5m outer diam. and >300kg segments (~all but small tactical missiles)
  - central port created by casting around mandrel
- **Free standing grains**
  - externally manufactured and cartridge loaded
  - can have inner and outer burning zones
  - reduced stress on propellant due to casing deformation
    - better suited for end burning motors (used in sustain portion of some missiles)

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

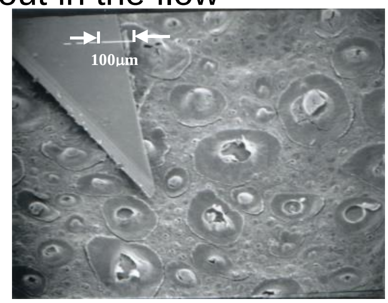
Solid Rocket Motors

Composite Propellants: Burning Rate – Limiting Processes

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Solid Composite Propellant Burning

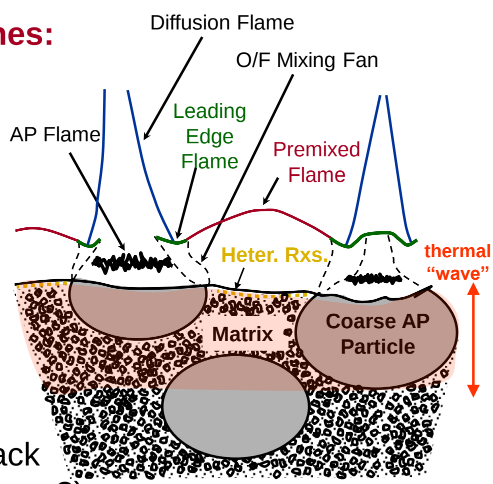
- Burning rate of the propellant is "driven" by chemical release of heat
- Heat release near the surface is more important than heat release further out in the flow



Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Propellant Flamelets - Price Model

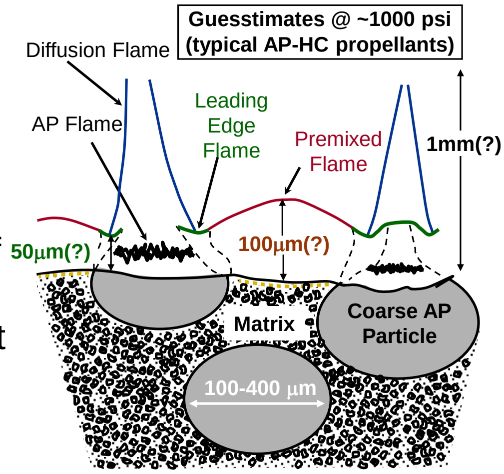
- **Five key reaction zones:**
  1. Premixed matrix flame
  2. AP monopropellant flame
  3. Diffusion flame (CAP and matrix)
  4. Leading Edge Flame (LEF)
  5. Near surface heterogeneous reactions (?)
- Final premixed flame too far away for feedback (except at very high press.?)



Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Propellant Flamelets - Dimensions

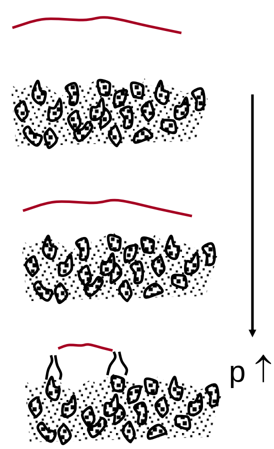
- Heat feedback and flame interaction depends on flame stand-off distances
- At practical pressures, standoff distances (even presence of distinct flame regions) are difficult to measure (too small)



Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Pressure Effects on Flamelet Location

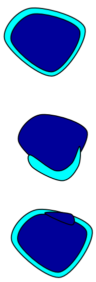
- Matrix flame
  - for low *p*, fine AP/binder gases mix together, get rich premix flame
  - premix flame speeds highly dependent on *p*
  - premixed flame (likely) get closer to matrix at higher *p*
  - eventually diffusion flames can take over (LEF's on fine AP)

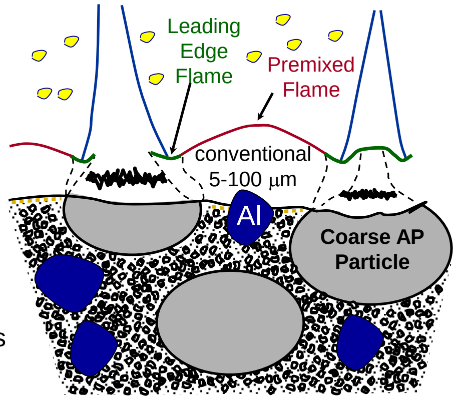


Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Aluminized Propellants

- Aluminum can oxidize rapidly if in contact with oxidizer
  – "burns" after melting
- But typical solid aluminum particles surround by (very thin) oxide "skin"
  – must be broached to burn Al rapidly
  – Al_2O_3 melts at ~2350K, would then pull back (surface tension)
  – can break if Al expands as it approaches Al melting (~933 K)
  – but surface temperature of propellants typically lower (e.g., 870 K, AP/HTPB)





⇒ Al usually needs to get closer to SP flame to burn
– can accumulate on surface
– can burn as detached droplet

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.

Some Current Issues

- AP replacement
- Designable plateau burning propellants
- Higher energetics with acceptable sensitivities
- "Nano" metals
- New manufacturing methods
  – stratified propellants
  – complex geometries
- Propellant combustion modeling

Copyright © 2009-2010, 2019 by Jerry M. Seitzman. All rights reserved.