Solid Rocket Motors

Solid Propellant Composition, Fabrication

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
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

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
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 ($KNO_3$)

**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%
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

Cleaved Propellant Sample

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

CP Ingredients – Oxidizers

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Density (kg/m³)</th>
<th>( Y_0 ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP</td>
<td>( \text{NH}_4\text{ClO}_4 )</td>
<td>1950</td>
<td>54.5</td>
</tr>
<tr>
<td>AN</td>
<td>( \text{NH}_4\text{NO}_3 )</td>
<td>1730</td>
<td>60.0</td>
</tr>
<tr>
<td>KP</td>
<td>( \text{KClO}_4 )</td>
<td>2520</td>
<td>46.2</td>
</tr>
<tr>
<td>KN</td>
<td>( \text{KNO}_3 )</td>
<td>2110</td>
<td>47.5</td>
</tr>
<tr>
<td>ADN</td>
<td>( \text{NH}_4\text{N(NO}_2)_2 )</td>
<td>1800</td>
<td>51.6</td>
</tr>
<tr>
<td>SN</td>
<td>( \text{NaNO}_3 )</td>
<td>2170</td>
<td>56.4</td>
</tr>
</tbody>
</table>

- Typically used inorganic oxidizers (normally 60-70%, <90% by mass)
  - perchlorates good oxidizers (AP most common) but HCl is product \( \Rightarrow \) 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)

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Solid Propellants

CP Ingredients – Binders

<table>
<thead>
<tr>
<th>Name</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU</td>
<td>Polaris</td>
</tr>
<tr>
<td>PBAN</td>
<td>polybutadiene acrylonitrile</td>
</tr>
<tr>
<td>PNC</td>
<td>plasticized nitrocellulose</td>
</tr>
<tr>
<td>CTPB</td>
<td>carboxy-terminated polybutadiene</td>
</tr>
<tr>
<td>HTPB</td>
<td>hydroxy-terminated polybutadiene</td>
</tr>
<tr>
<td>GAP</td>
<td>glycyl azide polymer (HC w/ O &amp; N(_3))</td>
</tr>
<tr>
<td>BAMO/AMMO</td>
<td>bis-azidomethylxetane/azido- methylxetane</td>
</tr>
</tbody>
</table>

- 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,...)
AP Example

- AP “oxidizer” can burn by itself at some pressures
- AP equilibrium composition at 1000 psi
  - $T_0 = 1400$ K
  - $\chi_{H_2O} = 38\%$
  - $\chi_{HCl} = 20\%$
  - $\chi_{N_2} = 12\%$
  - $\chi_{O_2} = 29\%$
- < 30\% of AP available as “oxidizer” for binder

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$_2$O$_4$, TiO$_2$, n-Butyl ferrocene, …
- Bonding agents, stabilizers, etc.

see Table 12-7 Sutton
**CP – Metallic Fuel Particles**

<table>
<thead>
<tr>
<th>MW</th>
<th>Density (kg/m³)</th>
<th>Tₚ₀ (K)*</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>27</td>
<td>2700</td>
<td>5170</td>
</tr>
<tr>
<td>Be</td>
<td>9</td>
<td>2300</td>
<td>5820</td>
</tr>
<tr>
<td>B</td>
<td>11</td>
<td>2400</td>
<td>4800</td>
</tr>
<tr>
<td>Mg</td>
<td>24</td>
<td>1750</td>
<td>---</td>
</tr>
<tr>
<td>Ti</td>
<td>48</td>
<td>4500</td>
<td>---</td>
</tr>
<tr>
<td>Zr</td>
<td>91</td>
<td>6400</td>
<td>---</td>
</tr>
</tbody>
</table>

- Also add metal particles/powders (~2-21%) *at 1000 psi with O₂
  - increase propellant density (reduce vol., incr. τ)
  - can increase Tₑ (c*, Iₛᵣ)
  - for some metals, product is liquid (Al₂O₃, BeO)
    - smoke, agglomeration and slagging, can’t expand in nozzle

**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
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

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
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)

Solid Rocket Motors

Composite Propellants: Burning Rate – Limiting Processes
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

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.?)
**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)

**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)
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
  - Al₂O₃ 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

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