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Combustion of Energetic Materials

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Combustion Characteristics of Solid Propellants

Description of Fuel Binders

- The binder provides the structural glue or matrix in which solid granular ingredients (like oxidizer particles and/or metal fuels) are held together in a heterogeneous (composite) propellant

- The binder raw materials are liquid prepolymers or monomers. After they are mixed with the solid ingredients, cast, and cured, they form a hard rubber-like material that constitutes the grain.

- In short, a prepolymer is a molecule formed by the repetition (in several orders of magnitudes) of a monomer form (butadiene, polypropylene oxide, etc.), generally ending with reactive functions (telechelic prepolymers). It is the prepolymer that confers on the binder its essential properties. These can be derived from the nature of the polymeric chain or the properties of the functional group at its ends.

- The molecular structure of polyether prepolymer is as follows:

$$H\text{-}(O\text{-}CH(CH_3)\text{-}CH_2)_n\text{-}O\text{-}CH_2\text{-}CH(CH_3)\text{-}O\text{-}(CH_2\text{-}CH(CH_3)\text{-}O)_n\text{-}H \quad n = 17$$

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

Description of Fuel Binders – cont'd

- A <u>curing agent or cross linker causes the prepolymers to form longer chains</u> of larger molecular mass and interlocks between chains (it causes the binder to solidify and become hard)

- <u>Polymerization occurs when the binder monomer and its cross linking agent react</u> (beginning in the mixing process) to form long chains and complex three-dimensional polymers

- The <u>binder ingredient has important influence</u> on *mechanical properties*, <u>propellant processing complexity</u>, <u>storability</u>, <u>aging</u>, and <u>costs</u>

Characteristics of GAP Binder

Glycidyl Azide Polymer

- GAP is an example of an energetic, thermally stable, hydroxyl-terminated prepolymer that can be polymerized [Sutton and Biblarz, 2017]

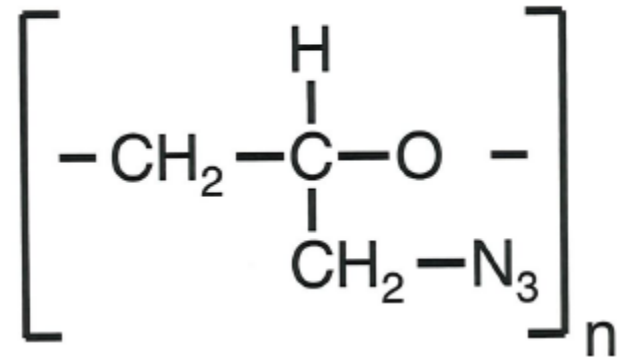- The GAP formulation is [Bathelt, Volk, and Weindel, 2001]

$C_3H_5N_3O$

Molecular weight: 99.092

Oxygen balance: -121.09%

Density: 1.29 gm/cm^3

Melting point: > 200°C

Enthalpy of formation: 141.0 kJ/mol (340.09 kcal/kg)

Characteristics of HTPB Binder

Hydroxyl Terminated Polybutadiene

- HTPB is the most common prepolymer binder material. It allows a high solid fraction (88 to 90% of AP and Al) and relatively good physical properties at the temperature limits [Sutton and Biblarz, 2017]
- There exist several different chemical formulae for HTPB. A typical one is [Bathelt, Volk, and Weindel, 2001]

$$\left[-CH_2-CH- \atop CH=CH_2 \right]_n \text{ resp. } \left[-CH_2-CH=CH-CH_2- \right]_n$$

$C_{10}H_{15.4}O_{0.07}$
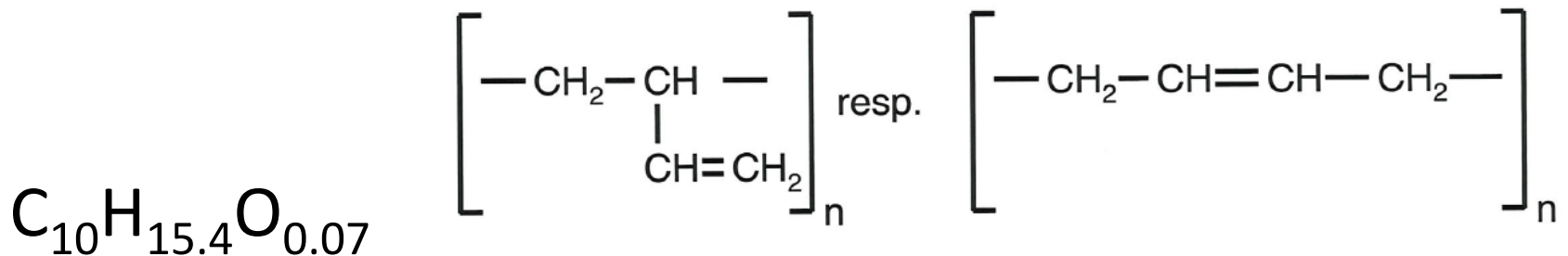
Molecular weight: 136.752 gm/mol

Oxygen balance: -323.026%

Density: 0.916 gm/cm^3

Melting point: 241°C

Enthalpy of formation: -51.88kJ/mol (-90.68 kcal/kg)

Some Properties of Fuel Binders

Binder	Chemical Formula	ΔH_f^0 [a] (kJ/mol)	T_{glass} (°C)	Oxygen Balance % [b]	Density (kg/m^3)	Impact sensitivity (Nm)
PLN[d]	$[C_5H_9NO_4]_n$	-334.7	-25[c]	-114.3	1260	>9
PGN[e]	$[C_3H_5NO_4]_n$	-284.5	-35[d]	-60.5	1390-1450	>20
HTPB	$[C_{10}H_{15.4}O_{0.07}]_n$	-51.9	-63	-323.8	916	>50
GAP	$[C_3H_5N_3O]_n$	117.2	-50	-121.2	1300	16->120
BAMO[f]	$[C_5H_8N_6O]_n$	413.0	-39	-123.8	1300	>20

[a] Values apply for n=1

[b] The oxygen balance is defined as the ratio of the mass of excess oxygen after complete conversion of the oxidizer into oxides(with the exception of nitrogen oxides) and the mass of the oxidizer

[c] By using suitable plasticizers, for PLN glass points as low as -63°C have been obtained

[d] PLN: poly-3-nitratomethyl-3-ethyloxetane, POLYNIMMO, or PN

[e] PGN: Polyglycidyl nitrate

[f] BAMO: 3,3'-Bis(azido methyl) oxetane

Desired Properties of a Binder

- The binder must be in <u>liquid form</u> during the preliminary phase of the preparation of the intimate mixture of oxidizer and fuel ingredients, although its elements must have sufficiently low volatility characteristics to withstand the high vacuum used during the mixing of the slurry and the casting of the propellant into a particular grain shape

- It must be <u>chemically compatible</u> with the oxidizer, which means that it will not cause even a slight temperature increase that may result in a exothermic reaction leading to any unwanted autoignition of the propellant

- It must be <u>capable of accepting very high solid loading ratios</u> (up to 80% in volume). The mixing operation must remain feasible, and the resulting slurry must be easily cast into shapes that are often complex and include some very narrow regions.

- The <u>mechanical properties</u> of the propellant <u>depend strongly on the selected binder</u>

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

Description of Curing and Cross Linking Agents

- A curing agent or cross linker <u>causes the prepolymers to form longer chains</u> of larger molecular mass and interlocks between chains. Even though these materials are present in small amounts (0.2 to 3%), a minor change in the percentage will have a major effect on the propellant physical properties, manufacturability, and aging.

- A curing agent and/or cross-linker are <u>used only with composite propellants</u>. These ingredients cause the binder to solidify and become hard [Sutton and Biblarz, 2001].

- The cross-linking agent in its most simple state could be a <u>poly-functional</u> molecule (frequently tri-functional) with a low molecular weight, or a mixture of bi-functional and tri-functional molecules. This approach can ensure an average functionality (i.e., number of reactive functions, divided by the total number of molecules) greater than 2 for the whole cross-linking system.

- The bi-functional molecules are generally called <u>chain extenders</u> and their role is to increase the length of the chain of pre-polymers

- Chemical reaction occurs between the prepolymer and the cross-linking agent after the polymer addition and the three-dimensional links are created [Davenas, 1993]

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

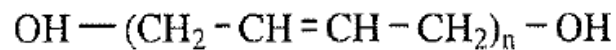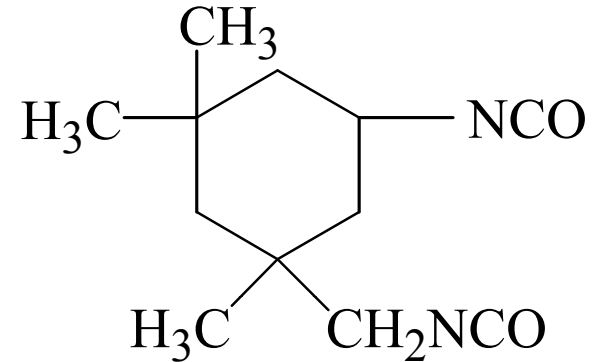# An example of a curing agent is isophorone diisocyanate (IPDI)

- $C_{12}H_{18}N_2O_2$

Molecular weight: 222.287 g/mol

Oxygen balance: -223.13%

Density: 1.061 gm/cm^3

Enthalpy of formation:

-372.00 kJ/mole (-399.98 kcal/kg)

$$OH - (CH_2 - CH = CH - CH_2)_n - OH \qquad + \qquad \textbf{IPDI Curative}$$

R-45 M Polymer
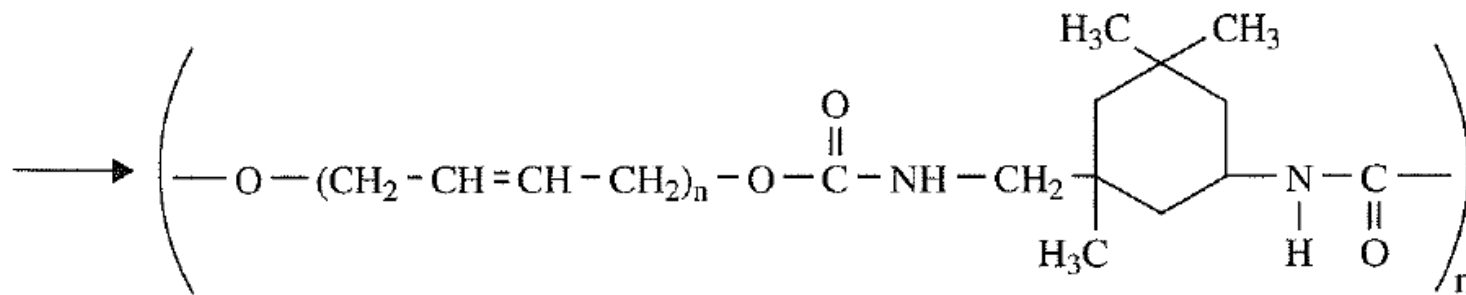
HTPB Binder

Desired Properties of a Curing Agent/Crosslinker

- After the slurry (mixed oxidizer and prepolymer) is in the casting mold, crosslinking must ensure its transformation into a solid through a chemical reaction obeying the following criteria [after Davenas, 1993]:

  - It must be a polyaddition reaction. Any elimination reaction producing more or less volatile products would result in the creation of cracks or "bubbles" in the crosslinked material. It is extremely important that the mixing of the slurry is conducted under vacuum to eliminate the gas present in soluble form in the binder. Otherwise, upon heating during the curing process, the gases dissolved in the slurry may lead to bubble or crack formation in the propellant.

  - This reaction must have on one hand a sufficiently slow cure kinetic rate to allow for the casting operations – this useful reaction time of several hours is also known as "pot-life" – and on the other hand must set sufficiently rapidly so as not to require lengthy crosslinking or curing times.

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Adapted From Kuo and Acharya, Turbulent and Multiphase Combustion, Wiley, 2012
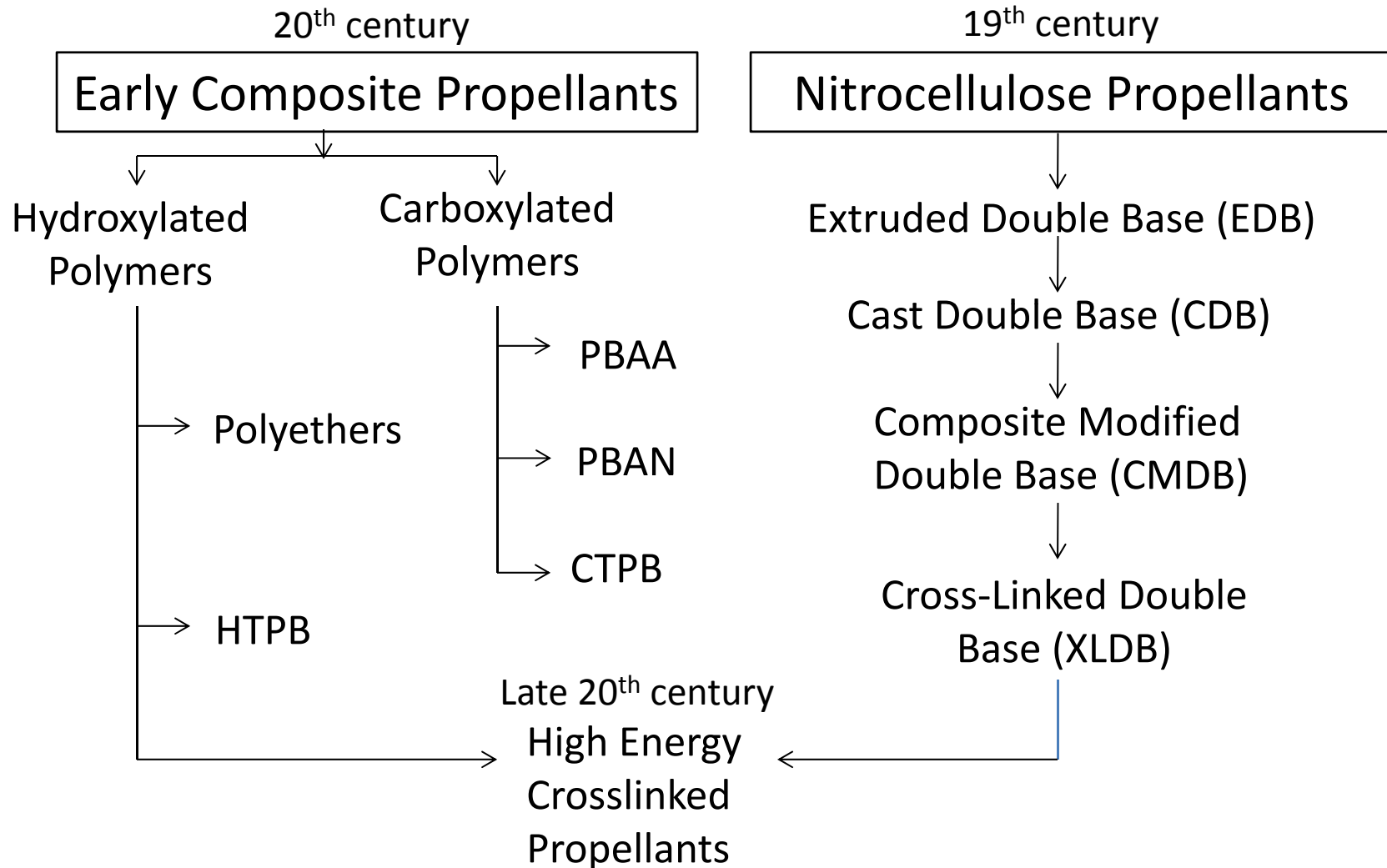
Desired Properties of a Curing Agent/Crosslinker

- The curing temperature cannot be too high, so as to prevent severe mechanical loads in case-bonded propellants.

- It must also be athermic (heatless), or not very exothermic, to avoid the release of heat inside the propellant grain, resulting in an increase of temperature inside this material, which is a poor heat conductor. This temperature increase could lead to mechanical loading conditions, possibly leading to cracks and autoignition of the propellant.

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

Definition of Aging

- Aging of solid propellants refers to the <u>deterioration of their physical properties with time</u>. It is <u>caused by the *cumulative damage*</u> done to the grain (such as by thermal cycling and load applications) during storage, handling, or transport. It can also be caused by chemical changes with time, such as the gradual depletion (evaporation) of certain liquid plasticizers or moisture absorption.

- The ability to carry stress or to allow elongation in propellants diminishes with cumulative damage. The <u>*aging limit*</u> is the estimated time when the energetic material is no longer able to perform its operation reliably or safely. Depending on the propellant and the grain design, this <u>age limit or motor life can be between 8 and 25 years</u> [Sutton and Biblarz, 2001].

- With small <u>rocket motors,</u> the aging limit is usually determined by full-scale motor firings at various time periods after manufacture, say <u>2 or 3 years</u>. Accelerated temperature aging (more severe thermal cycles) and accelerated mechanical pulse loads and overstressing are often used to reduce the time needed for these tests [Sutton and Biblarz, 2001].

- Rocket motor <u>aging refers</u> not only to the propellant, but also <u>to other components</u> such as: igniter pyrotechnic charge, initiator material, O-rings and other organic material, and metals (corrosion).

Family Tree of Double-Base and Composite Propellants with High-Energy Cross-Linked Propellants

20th century

19th century

Early Composite Propellants

Nitrocellulose Propellants

Hydroxylated Polymers

Carboxylated Polymers

Extruded Double Base (EDB)

Cast Double Base (CDB)

Polyethers → PBAA

→ PBAN

Composite Modified Double Base (CMDB)

→ CTPB

HTPB

Cross-Linked Double Base (XLDB)

Late 20th century High Energy Crosslinked Propellants

After A. Devanas, Journal of Propulsion and Power, 19, 6, 2003

Six Families of Propellants are Commonly Manufactured

1. Extruded double base (**EDB**) are prepared by impregnation of NC with NG in a water medium to get a paste, followed by kneading with additives and carpet rolling at an elevated temperature. The final configuration is obtained by extrusion through a die.

2. Cast double base propellants (**CDB**) are similar to EDB and are obtained by casting a mixture of NG and inert plasticizer into a mold containing a NC-based powder with various additives. The casting solvent swells and dissolves the NC through curing. They have less size limitations and allow 3-D shapes.

3. Composite modified double base (**CMDB**) are derived from CDB by addition of energetic solids, and generally nitrogylcerine in the casting powder

4. Elastomeric modified double base (**EMCDB**) have better mechanical properties than CDB by modifications in the liquid casting solvent

5. Composite propellants are based on a nonenergetic polymeric binder and high levels of AP, and can contain aluminum

6. High energy propellants are sometimes called cross-linked double base (**XLDB**) even though there may not be any NC in binder. Production and physical behavior similar to composite propellants, but with a special preparation of energetic binder elements.

Propellant – Density Calculation [gm/cm³]

Propellant density [gm/cm³]

Mass fraction of jth component

$$\rho_{propellant} = \frac{1}{\sum_{j=1}^{NC} \frac{Y_j}{\rho_j}}$$

(2)

Number of components

Density of jth component [gm/cm³]

Examples:

Component	Name	Mass Fraction	ρ, gm/cm³	
1	HTPB	0.12	0.918	$\rho_{propellant}$ = 1.718 gm/cm³
2	AP	0.88	1.950	

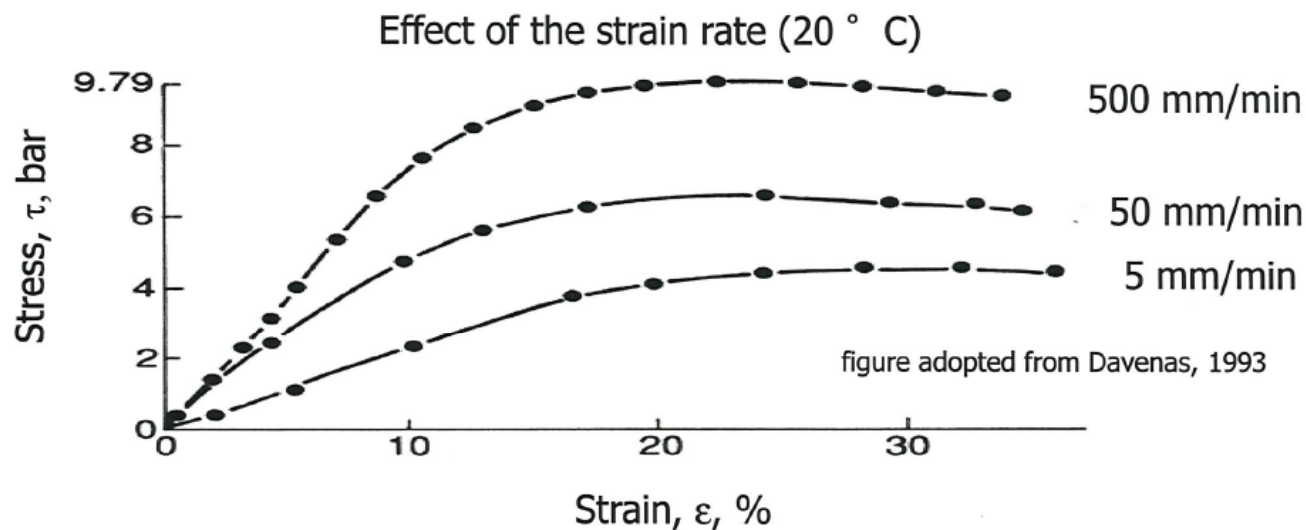| Component	Name	Mass Fraction	ρ, gm/cm³	
1	HTPB	0.12	0.918	
2	AP	0.70	1.950	$\rho_{propellant}$ = 1.797 gm/cm³
3	Al	0.18	2.700	

Propellant Mass Fraction, Λ

- The propellant mass fraction, Λ, is a measure of motor design loading efficiency. It is usually defined as the ratio of the mass of initial propellant to the mass of the total rocket motor, where the total motor consists of the initial propellant plus motor inert components (motor case, nozzle assembly, etc.)

$$\Lambda \equiv \left. \frac{m_{\text{propellant}}}{m_{\text{rocket motor}}} \right|_{t=0} \tag{3}$$

- Solid propellant mass fractions vary from about 0.3 to 0.96. The lower values apply to auxiliary motors, gas generators, and very small motors and the high mass fractions with simple motors and particularly with upper stage motors

Material Characteristics of Propellants

- The propellant is a rubber like material that is nearly incompressible. Usually, there are very few voids (<< 1%) in a properly made propellant. However, the propellant is easily damaged by applied tension and shear loads. These types of stress loads can cause damage due to "dewetting" of the adhesion between individual oxidizer particles and the binder material surrounding them. Under vacuum conditions, very small voids could exist next to the oxidizer particles. These voids could become larger with an increase of shear or tensile strains.

- The propellant shows a nonlinear viscoelastic behavior $\tau = f\left(\varepsilon, \dfrac{d\varepsilon}{dt}\right)$

Effect of the strain rate (20 °C)

500 mm/min

50 mm/min

5 mm/min

figure adopted from Davenas, 1993

Stress, τ, bar

Strain, ε, %

Material Characterization of Propellants (cont'd)

- The non-linear mechanical behavior means that the stress response of the propellant depends on both the level of strain applied and the strain rate at which it is applied

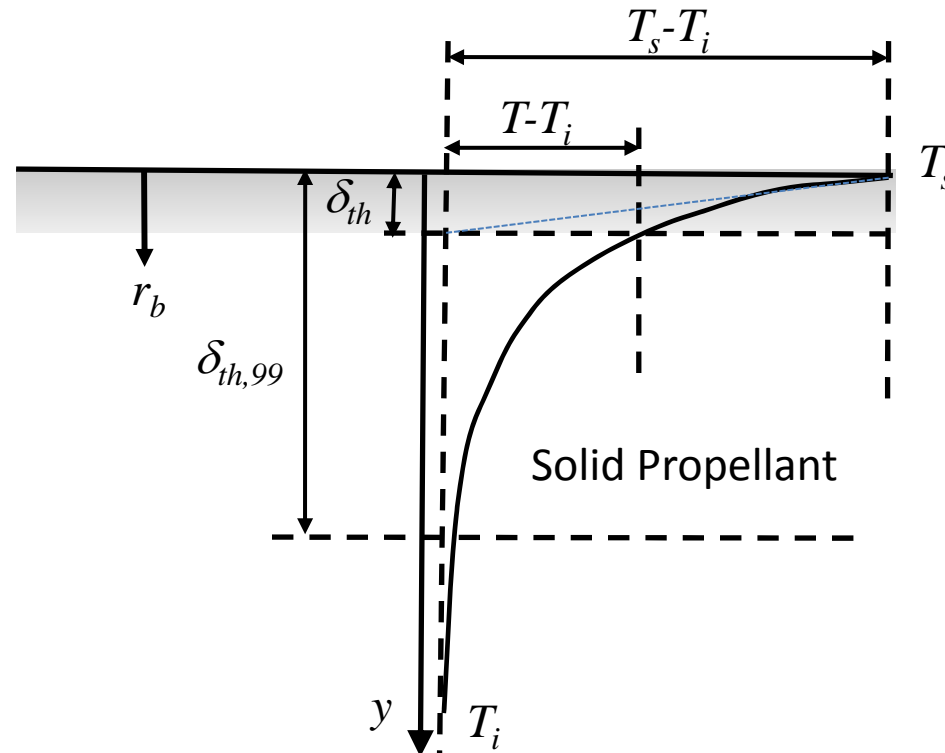$$\tau = f\left(\varepsilon, \frac{d\varepsilon}{dt}\right) \tag{4}$$

- Also, the maximum stress and maximum elongation (or strain) diminish each time a significant load is applied. The material becomes weaker and suffers some damage with each loading cycle or thermal stress application [Sutton and Biblarz, 2017]

- The mechanical properties are also a function of the initial temperature of the propellant

Surface Temperature Measurement of Solid Propellants

- For a steady-state burning solid propellant, the temperature profile can be given as:

$$\theta \equiv \frac{T - T_i}{T_s - T_i} = exp\left(-\frac{\dot{m}_p C_c y}{k_p}\right) = exp\left(-\frac{\rho_p r_b C_c y}{k_p}\right) = exp\left(-\frac{r_b y}{\alpha_p}\right) \quad (5)$$

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

Surface Temperature Measurement of Solid Propellants cont'd

- The thermal wave thickness can be defined as:

$$\delta_{th} = \alpha_p / r_b \tag{6}$$

  which represents a depth at which the tangent line to the temperature profile (at $y = 0$) intersects with the initial temperature profile and is the depth in the solid where $\theta = 0.368$

- Another definition for the thermal wave thickness $\delta_{th,99}$ can be defined as the depth in the solid where $\theta = 0.01$. Usually
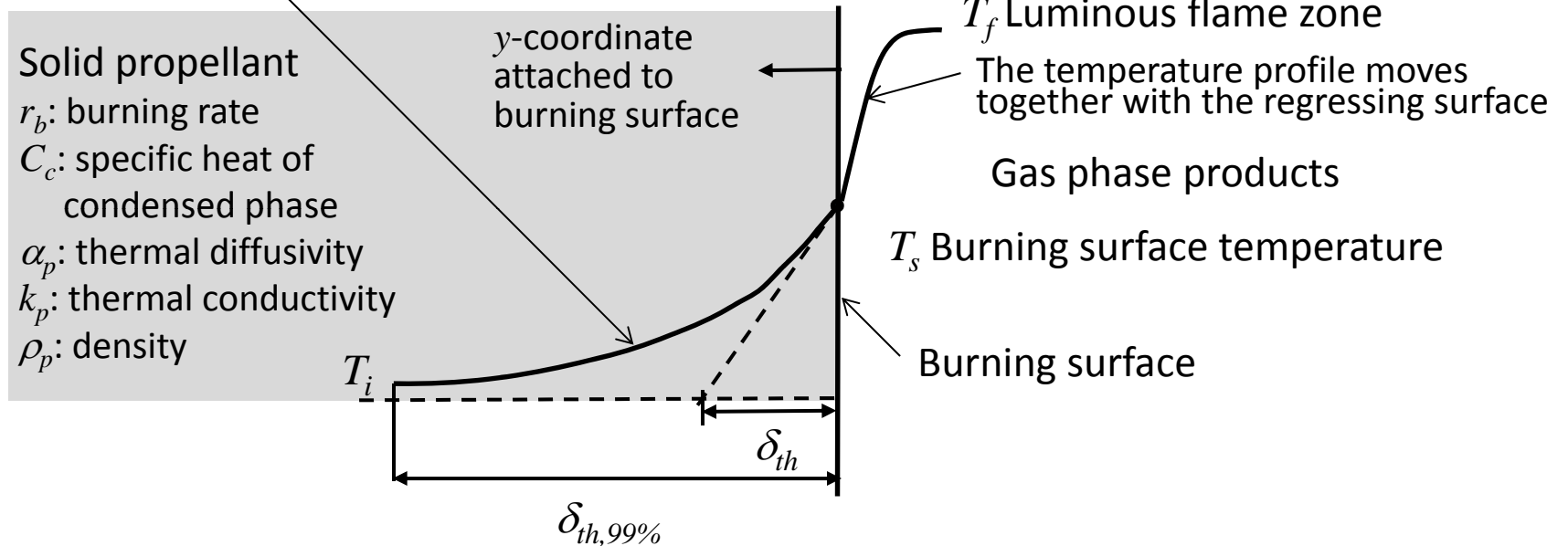
$$\delta_{th,99} = 4.605\ \delta_{th} \tag{7}$$

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

Surface Temperature Measurement of Solid Propellants (cont'd)

- The sub-surface temperature profile of a burning propellant can be measured using a fine-wire thermocouple embedded in a propellant strand specimen.

- In order to achieve a lower measurement error, the thermocouple size must be much smaller than the thermal wave thickness.

- This means that the thermocouple bead size (or thickness) should be smaller than $0.2\alpha_p/r_b$, where α_p is the propellant thermal diffusivity and r_b the burning rate.

- For example, a typical propellant has $\alpha_p = 1.8$ x 10^{-3} cm^2/s and if $r_b = 1$ cm/s then $0.2\alpha_p/r_b = 3.6$ μm, while $\delta_{th,99} = 83$ μm.

Thermal Wave Thickness δ_{th}

$$\frac{T(y) - T_i}{T_S - T_i} = exp\left(-\frac{r_b y}{\alpha_p}\right) \qquad \alpha_p = \frac{k_p}{\rho_p C_c}$$

Solid propellant
r_b: burning rate
C_c: specific heat of
    condensed phase
α_p: thermal diffusivity
k_p: thermal conductivity
ρ_p: density

T_i

y-coordinate attached to burning surface

T_f Luminous flame zone

The temperature profile moves together with the regressing surface

Gas phase products

T_s Burning surface temperature

Burning surface

δ_{th}

$\delta_{th,99\%}$

$$\frac{dT}{dy} = -\frac{T_S - T_i}{\alpha_p / r_b} exp\left(-\frac{r_b y}{\alpha_p}\right) \Rightarrow \left.\frac{dT}{dy}\right|_{y=0} = -\frac{T_S - T_i}{\alpha_p / r_b} = \frac{T_S - T_i}{\delta_{th, tangent}} \Rightarrow \delta_{th} \equiv \delta_{th, tangent}$$

$$\delta_{th} = \frac{\alpha_p}{r_b} \quad \text{and} \quad \delta_{th, 99\%} = 4.6\frac{\alpha_p}{r_b}$$

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

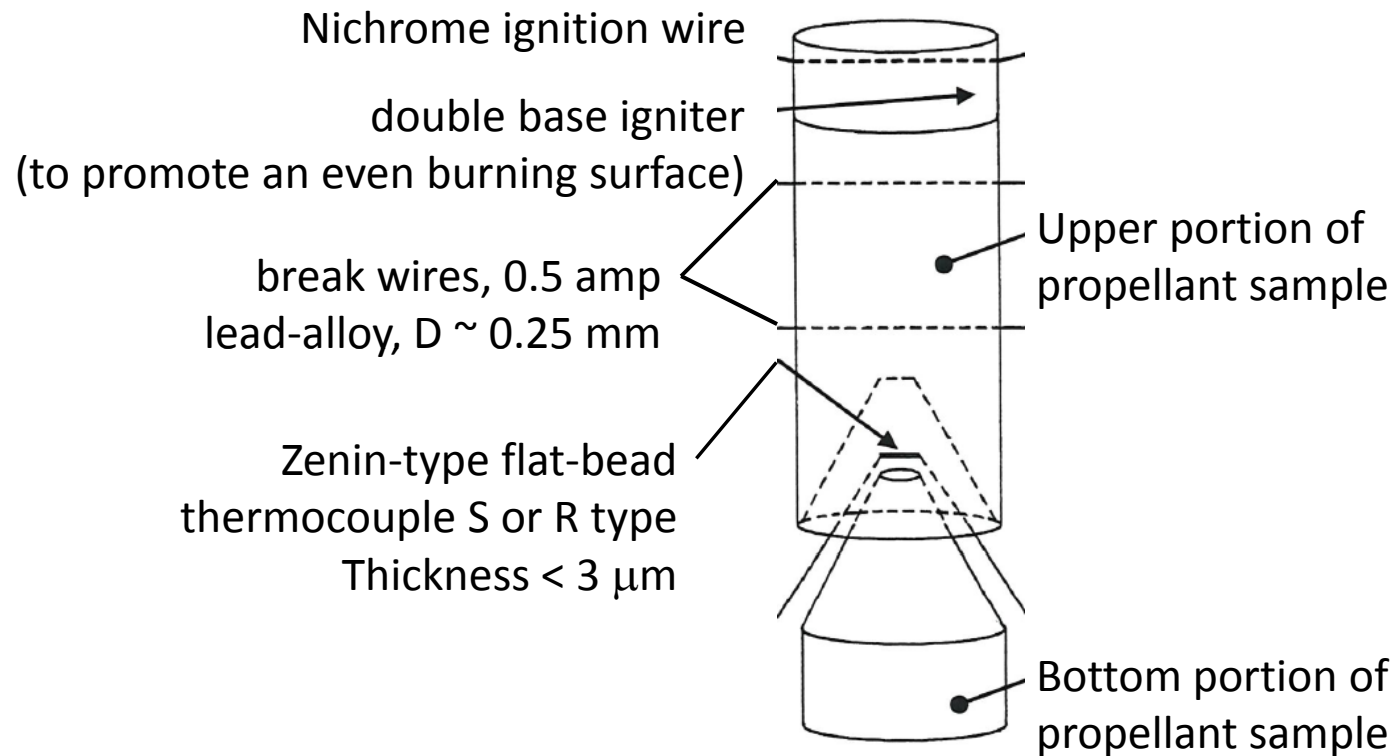# Example of thermal wave thickness in a composite propellant

$$\left.\begin{array}{l} \rho_p = 1700 \text{ kg/m}^3 \\ C_c = 1465 \text{ J/kg-K} \\ k_p = 0.21 \text{ W/m-K} \end{array}\right\} \Rightarrow \alpha_p = 0.84 \times 10^{-3} \text{ cm}^2/\text{s}$$

$$r_b = 1 \text{ cm/s}$$

$$\Rightarrow \delta_{th,99\%} = 39 \ \mu\text{m}$$

Thus, the thermocouple size should be 1 – 2 μm thick

- Typical ammonium perchlorate (AP) particles range in size from 40 μm to 200 μm
- δ_{th} is on the same order as AP particle size
- This implies that the heat transfer process in AP composite propellants is essentially 3-D

A Method for Inserting a Flat-Bead Thermocouple into Propellant Strand

Nichrome ignition wire

double base igniter
(to promote an even burning surface)

break wires, 0.5 amp
lead-alloy, D ~ 0.25 mm

Zenin-type flat-bead
thermocouple S or R type
Thickness < 3 μm

Upper portion of
propellant sample

Bottom portion of
propellant sample

- Usually, an S-type of thermocouple (TC) made of Platinum (Pt) and Pt with 20% Rhodium (Rh) can be used for sub-surface temperature measurement in a propellant strand
- For higher temperatures, a D-type of TC made of Tungsten (W) and Rhenium (Re) can be used, which can measure temperatures as high as 2593 K

Thermocouple trace for a HTPB solid fuel grain burning with O_2
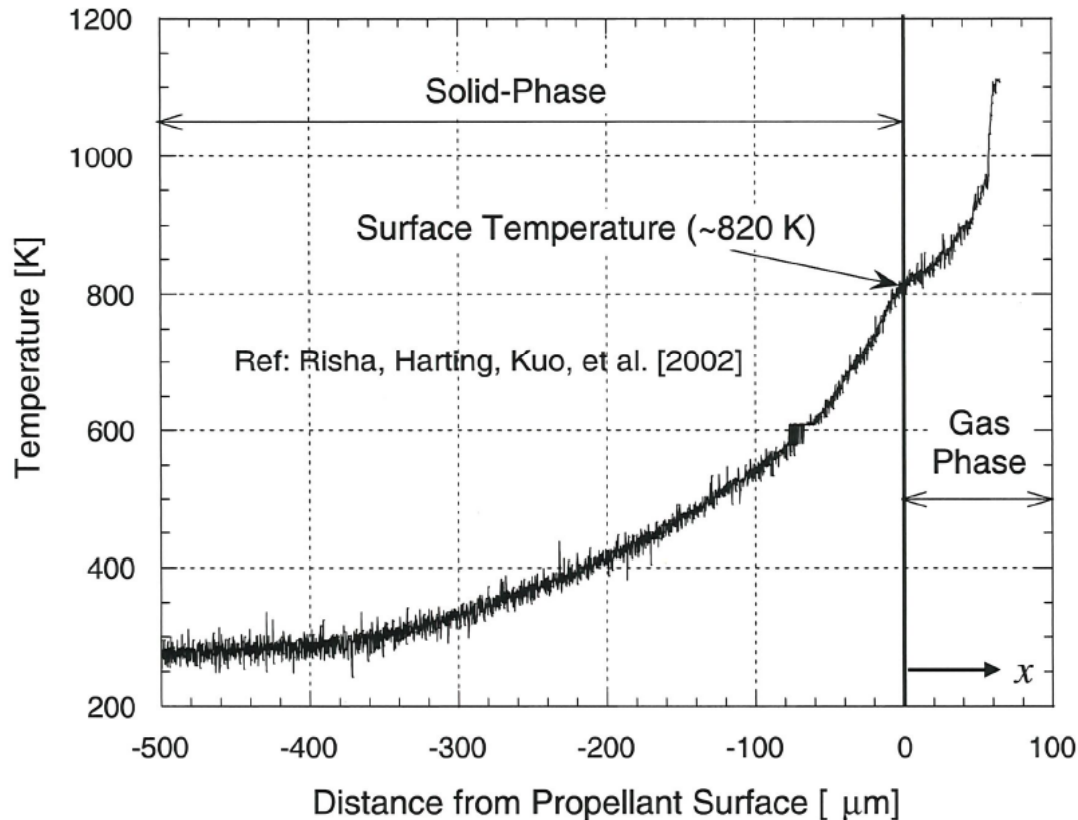
- The thermal wave thickness is several hundred μm at a regression rate of 0.45 mm/s
- At the interface, the energy balance can be written as:

$$k_p \left.\frac{dT}{dx}\right|_{0^-} = k_g \left.\frac{dT}{dx}\right|_{0^+} + \rho_p r_b Q_s \quad (8)$$

where Q_s = net heat release at the surface

- The slope change at the surface varies depending upon the magnitude of net energy release per unit surface area

$$Q_s\left[kJ/kg\right] = 43.34\left(r_b\left[mm/s\right]\right)^{-1.59} \quad (9)$$

- If $\rho_p r_b Q_s$ term is high enough then the slope of temperature profile in the gas phase could be less steep

Surface Temperature Measurement of Solid Propellants (cont'd)

The surface temperature T_s is determined at the location of the point of departure from the linear behavior on a semi-natural log plot of temperature versus distance.

Propellant burning surface location

$$\frac{T(y) - T_i}{T_s - T_i} = exp\left(-\frac{r_b y}{\alpha_p}\right)$$

$$\Downarrow$$

$$ln\left(\frac{T(y) - T_i}{T_s - T_i}\right) = -\frac{r_b y}{\alpha_p}$$

$$\Downarrow$$

$$ln(T(y) - T_i) = ln(T_s - T_i) - \frac{r_b y}{\alpha_p}$$

$$\Downarrow$$
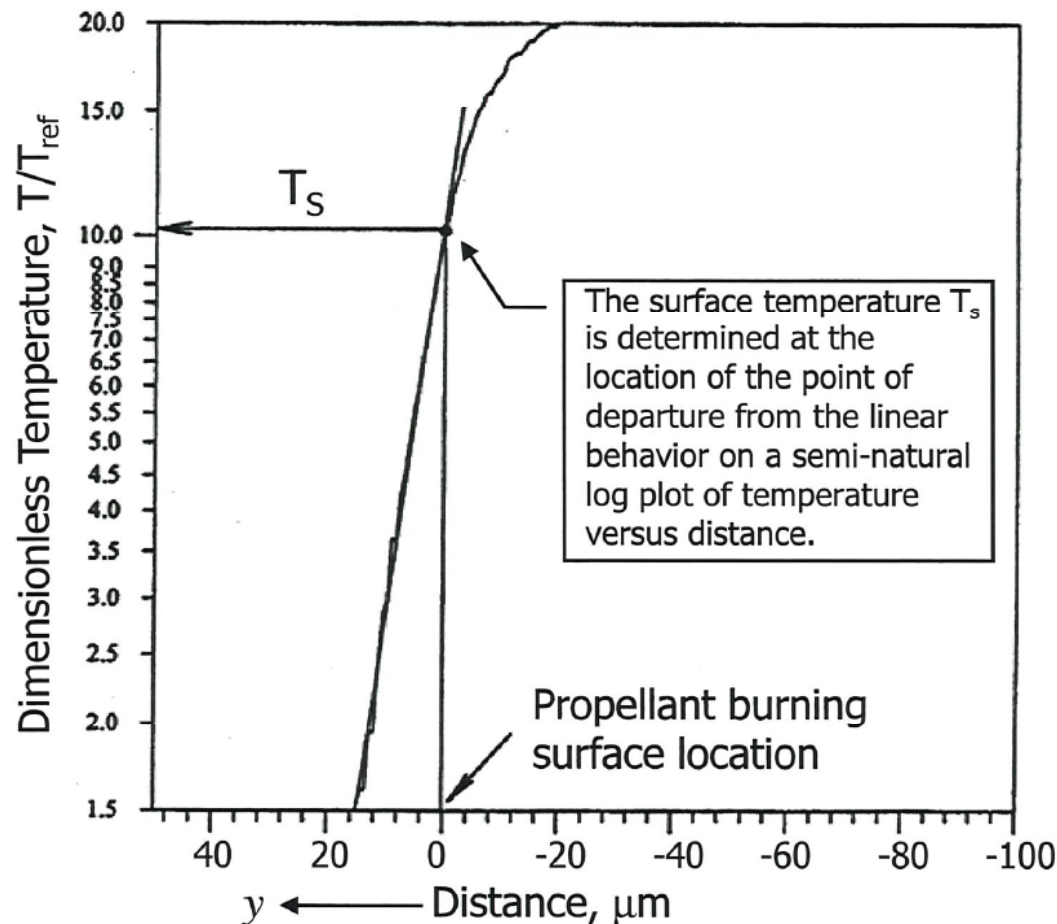
$$ln\left(\frac{T}{T_{ref}}\right) \propto y \qquad (10)$$

A linear relationship, with $T_i = T_{ref}$

Thermal Diffusivity, α – Definition [m²/s]
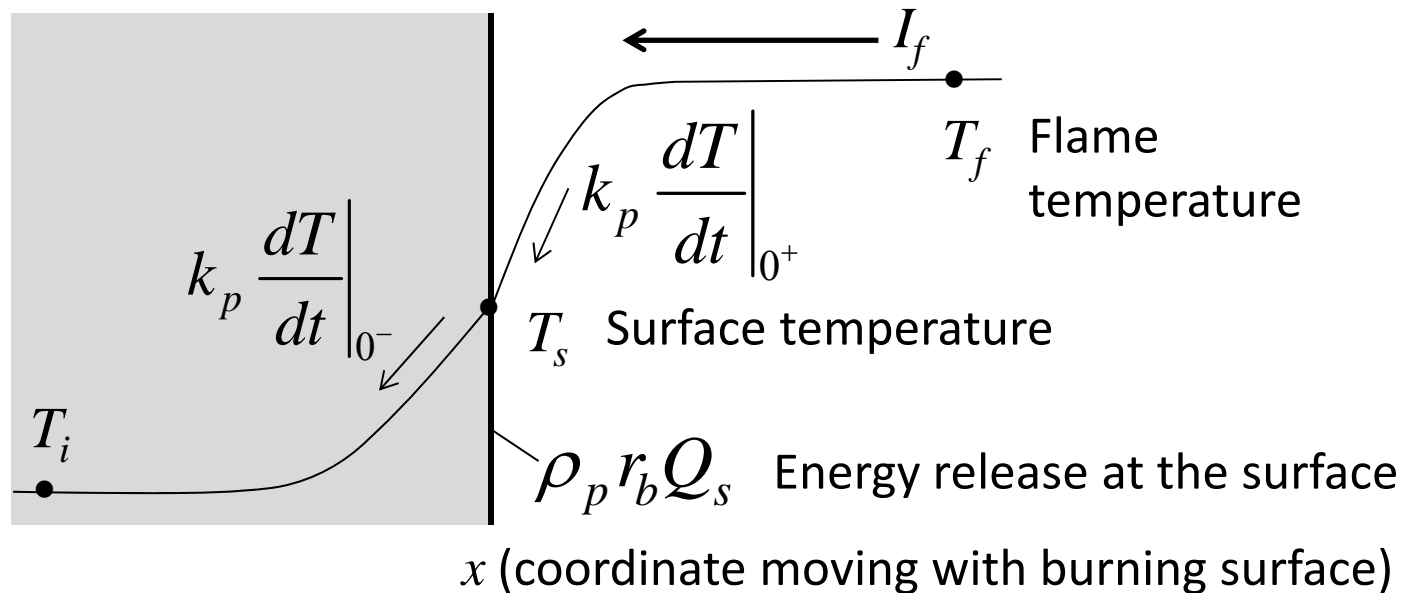
- The ratio of the thermal conductivity to the product of density and heat capacity is an important property termed the thermal diffusivity α, which has units of m²/s

- It measures the ability of a material to conduct thermal energy relative to its ability to store thermal energy. Materials of large α will respond quickly to changes in their thermal environment, while materials of small α will respond more slowly to reach a new equilibrium condition.

$$\alpha = \frac{k}{\rho C} \qquad k - \text{thermal conductivity, } \rho - \text{density, } C - \text{specific heat} \qquad (11)$$

- Thermal properties of several materials are listed below:

	ρ [kg/m³]	C [J/kg-K]	k [W/m-K]	α [m²/s]
Al 2024	2770	875	177	73
Stainless steel AISI 302	8055	480	15	3.91
Composite propellant	1700	1400	0.4	0.17
JA2 propellant	1570	1342	0.278	0.132

Energy Flux Balance at Interface

I_f

$k_p \left.\dfrac{dT}{dt}\right|_{0^+}$

T_f Flame temperature

$k_p \left.\dfrac{dT}{dt}\right|_{0^-}$

T_s Surface temperature

T_i

$\rho_p r_b Q_s$ Energy release at the surface

x (coordinate moving with burning surface)

C_c = condensed phase specific heat, r_b = propellant burning rate

T = temperature

Q_s = heat of reaction at the surface per unit mass,

k_p = propellant thermal conductivity,

k_g = gas thermal conductivity, and

ρ_p = propellant density

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

Energy Flux Balance at Interface

- Energy flux balance at the propellant surface can be expressed as:

$$k_p \left[\frac{dT}{dx} \right]_{0^-} = k_g \left[\frac{dT}{dx} \right]_{0^+} + \rho_p r_b Q_s + I_f \qquad (12)$$

$\underbrace{\phantom{k_p \left[\frac{dT}{dx} \right]_{0^-}}}$ Heat flux into the sub-surface region at y = 0⁻ by conduction

$\underbrace{\phantom{k_g \left[\frac{dT}{dx} \right]_{0^+}}}$ Heat flux from gas-phase to burning surface at y = 0⁺ by conduction

$\underbrace{}$ Heat released at y = 0 due to chemical reaction at surface

$\underbrace{}$ Heat feedback from the flame zone to the surface by radiation or external radiative energy source
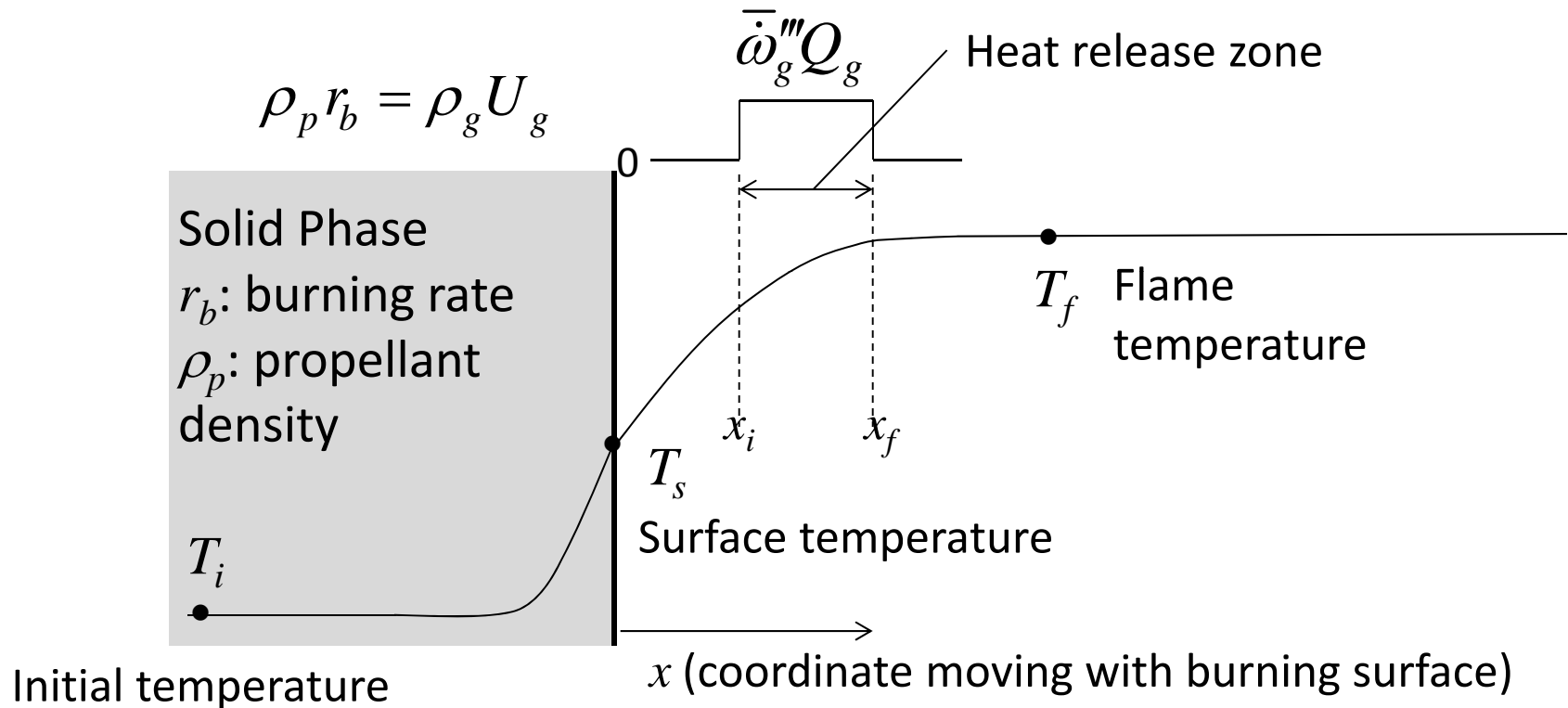
- If there are no subsurface reactions, then:

$$k_p \left[\frac{dT}{dx} \right]_{0^-} = \rho_p r_b C_c \left(T_s - T_i \right) \qquad (13)$$

- Assuming that I_f is very small in the flux balance equation and utilizing the above relationship, we have:

$$k_g \left[\frac{dT}{dx} \right]_{0^+} = \rho_p r_b \left[C_c \left(T_s - T_i \right) - Q_s \right] \qquad (14)$$

Energy Equation for Gas Phase

$$\rho_p r_b = \rho_g U_g$$

$$\overline{\dot{\omega}}_g''' Q_g$$

Heat release zone

0

Solid Phase

r_b: burning rate

ρ_p: propellant density

T_i

T_s

x_i x_f

T_f Flame temperature

Surface temperature

Initial temperature

x (coordinate moving with burning surface)

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

Energy Equation for Gas Phase

- The 1-D gas-phase energy equation is:

$$\frac{d}{dx}\left(k_g\frac{dT}{dx}\right) - \rho_g U_g C_{pg}\frac{dT}{dx} + \dot{\omega}_g''' Q_g = 0 \qquad (15)$$

- If k_g and C_{pg} are independent of temperature

$$k_g\frac{d^2T}{dx^2} - \rho_g U_g C_{pg}\frac{dT}{dx} + \dot{\omega}_g''' Q_g = 0 \qquad (16)$$

- Assuming $\dot{\omega}_g''' Q_g$ is constant starting from x_i to x_f and zero elsewhere, we can integrate the above equation as follows:

$$k_g\left[\frac{dT}{dx}\right]_{0^+} = Q_g \int_0^\infty exp\left(-\frac{\rho_g U_g C_{pg}}{k_g}x\right)\dot{\omega}_g''' dx \qquad (17)$$

provided

$$\dot{\omega}_g''' Q_g = \begin{cases} 0 & 0 < x < x_i \\ \overline{\dot{\omega}}_g''' Q_g & x_i < x < x_f \\ 0 & x_f < x < \infty \end{cases}$$

Energy Equation for Gas Phase

At $x=x_i$, exothermic reaction starts and at $x=x_f$ heat release zone ends

$$k_g\left[\frac{dT}{dx}\right]_{0+} = \frac{k_g}{\rho_g U_g C_{pg}}\bar{\dot{\omega}}'''Q_g\left\{\exp\left(-\frac{\rho_g U_g C_{pg}}{k_g}x_i\right)-\exp\left(-\frac{\rho_g U_g C_{pg}}{k_g}x_f\right)\right\}$$

The reaction zone thickness, $\delta_{flame} = x_f - x_i$

If the reaction starts at the surface, i.e., $x_i = 0$:

$$k_g\left[\frac{dT}{dx}\right]_{0+} = \frac{k_g}{\rho_g U_g C_{pg}}\bar{\dot{\omega}}'''_g Q_g\left[1-\exp\left(-\frac{\rho_g U_g C_{pg}x_f}{k_g}\right)\right] \qquad (18a)$$

If $\left(\dfrac{\rho_g U_g C_{pg}x_f}{k_g}>>1\right)$,

then $k_g\left[\dfrac{dT}{dx}\right]_{0+} \cong \dfrac{k_g}{\rho_g U_g C_{pg}}\bar{\dot{\omega}}'''_g Q_g \cong \dfrac{k_g}{\rho_p r_b C_{pg}}\bar{\dot{\omega}}'''_g Q_g \qquad (18b)$

Energy Equation for Gas Phase

For <u>extremely thin reaction zone</u> located at $x = x_f$ (i.e., the flame-sheet case), reaction rate in the gas-phase can be expressed as

$$\int_0^\infty \overline{\dot{\omega}}_g''' \delta\left(x - x_f\right) dx = \rho_g U_g \qquad (19)$$

where, δ is the Dirac-delta function.

Substituting above relationship into the heat-flux balance equation at $x = 0^+$, we get

$$k_g \left[\frac{dT}{dx}\right]_{0+} = Q_g \int_0^\infty exp\left(-\frac{\rho_g U_g C_{pg}}{k_g} x\right) \overline{\dot{\omega}}_g''' \delta\left(x - x_f\right) dx \qquad (20)$$

or

$$k_g \left[\frac{dT}{dx}\right]_{0+} = \rho_g U_g Q_g \, exp\left(-\frac{\rho_g U_g C_{pg}}{k_g} x_f\right) = \rho_p r_b Q_g \, exp\left(-\frac{\rho_p r_b C_{pg}}{k_g} x_f\right)$$

$$(21)$$

Burning Rate of Solid Propellants

r_b can be determined by using Eqs. (12), (13), and (18b).

$$\underbrace{k_p\left[\frac{dT}{dx}\right]_{0^-}}_{\substack{\text{Heat flux into the}\\\text{sub-surface region}\\\text{at y=0}^-\text{by conduction}}} = \underbrace{k_g\left[\frac{dT}{dx}\right]_{0^+}}_{\substack{\text{Heat flux from gas-phase}\\\text{to burning surface at y=0}^+\\\text{by conduction}}} + \underbrace{\rho_p r_b Q_s}_{\substack{\text{Heat released at}\\\text{y=0 due to chemical}\\\text{reaction at surface}}} + \underbrace{I_f}_{\substack{\text{Heat feedback}\\\text{from the flame}\\\text{zone to the surface}\\\text{by radiation or external}\\\text{radiative energy source}}} \quad (12)$$

$$k_p\left[\frac{dT}{dx}\right]_{0^-} = \rho_p r_b C_c (T_s - T_i) \quad (13)$$

When the heat-release zone starts from $x=0^+$

$$k_g\left[\frac{dT}{dx}\right]_{0+} = \frac{k_g}{\rho_p r_b C_{pg}} \overline{\dot{\omega}}_g''' Q_g \quad (18b)$$

By substituting Eqs. (13) and (18b) into Eq. (12) and re-arranging, we have:

$$r_b = \left[\frac{k_g \overline{\dot{\omega}}_g''' Q_g}{\rho_p^2 C_{pg}\left[C_c(T_S - T_i) - Q_S\right]}\right]^{1/2} \approx \left(\overline{\dot{\omega}}_g''' Q_g\right)^{1/2} \quad (22)$$

Burning Rate of Solid Propellant *(cont.)*

Generally, the reaction rate of a one-step forward reaction

$$\sum_{i=1}^{N} v_i' M_i \xrightarrow{\ k_f\ } \sum_{i=1}^{N} v_i'' M_i \qquad (23)$$

with N = total no. of species (reactants + products)

is represented by

$$\underbrace{\dot{\omega}_g'''}_{\substack{\text{Mass} \\ \text{generation} \\ \text{rate per} \\ \text{volume}}} = \underbrace{\left(\underbrace{\sum v_i''}_{\text{products}} - \underbrace{\sum v_i'}_{\text{reactants}} \right)}_{\substack{=\Delta n = \text{Difference} \\ \text{in stoichiometeric} \\ \text{coefficients between} \\ \text{product \& reactant species}}} \underbrace{k_f}_{\substack{\text{Reaction} \\ \text{rate} \\ \text{constant}}} \prod_{k=1}^{N} \underbrace{\left(\rho_g \right)^{v_k'}}_{\substack{\text{Gas} \\ \text{density}}} \underbrace{\left(X_k \right)^{v_k'}}_{\substack{\text{Mole} \\ \text{fraction}}} \qquad (24)$$

Burning Rate of Solid Propellant *(cont.)*

Therefore, substituting the above expression into Eq. (22), we have:

$$r_b = \left[\frac{k_g Q_g \Delta n \, k_f \prod_{k=1}^{N} \left(\rho_g X_k \right)^{v_k'}}{\rho_p^2 C_{pg} \left[C_c \left(T_S - T_i \right) - Q_s \right]} \right]^{1/2} \quad (25)$$

Generally, the gas-phase reactions in the burning of energetic materials are bimolecular and of second order, i.e., the number of reactants (*F* and *O*) = 2 and $v_F' = v_O' = 1$,

$$r_b = \left[\frac{\left(k_g Q_g \Delta n \, k_f \rho_g^2 X_F X_O \right)}{\left\{ \rho_p^2 C_{pg} \left[C_c \left(T_S - T_i \right) - Q_s \right] \right\}} \right]^{1/2} \quad (26)$$

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

Burning Rate of Solid Propellants *(cont.)*

- The reaction rate constant, k_f, is a function of gas temperature and is expressed in Arrhenius form as following:

$$k_f = A_g \, exp\left(-E_{a,g}/R_u T_g\right) \qquad (27)$$

- Under low pressure conditions, the ideal gas law can be used to relate the gas density ρ_g with pressure p and gas temperature T_g by $\rho_g = p/RT_g$ $\qquad$ (28)

- Substituting Eqs. (27) and (28) into Eq. (26), we have:

$$r_b = p\left[\frac{k_g Q_g \Delta n \, X_F \, X_O A_g \, exp\left(-E_{a,g}/R_u T_g\right)}{\left(RT_g\right)^2 \rho_p^2 C_{pg}\left[C_c\left(T_s - T_i\right) - Q_s\right]}\right]^{1/2} \qquad (29)$$

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

Burning Rate of Solid Propellants *(cont.)*

- Another way to express the burning rate of a solid propellant is by relating its burning surface temperature using an Arrhenius equation; i.e.,

$$r_b = A_s T_s^{\beta} \, exp\left(-E_{a,s}/R_u T_s\right) \qquad (30)$$

- The burning rate of a solid propellant is also given by Saint-Robert's law (or Vieille's law) as:

$$r_b = ap^n \qquad (31)$$

- At very high pressures, the linear form of burning rate is sometimes used (known as Muraour's law):

$$r_b = b_1 + b_2 p \qquad (32)$$

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