

Propellant Chemistry

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ABSTRACT

Propellants used for pyrotechnics are composed of energetic materials that produce high-temperature and high-pressure gaseous products. The propellants are classified into three types by their physical structure and the ingredients used: (1) homogeneous propellants consisting of chemically bonded oxidizer and fuel components in the same molecule, (2) heterogeneous propellants consisting of physically mixed oxidizer and fuel components, and (3) granulated propellants consisting of energetic solid particles. While the energy content of a propellant is determined by the chemical properties of the ingredients, the physical properties and chemical processes of the ingredients determine the ballistic characteristics such as burn rate and pressure and temperature sensitivities.

Keywords: propellant chemistry, activation energy, burn rate

Nomenclature

a = burn rate constant defined in equation 8
 A_b = burn area, m^2
 A_t = nozzle throat area, m^2
 c = specific heat, kJ/kgK
 c_d = mass discharge coefficient
 c_f = thrust coefficient
 d = dark zone pressure exponent
 E = activation energy, $kJ/kmol$
 H_{exp} = heat of explosion, MJ/kg
 I = radiative heat flux, kW/m^2
 k = reaction order
 K_n = area ratio defined by A_b/A_t
 m = mass flow rate, kg/m^2s or reaction order in the dark zone
 m_d = mass discharge rate, kg/s

m_g = mass generation rate, kg/s
 M = molecular mass, $kg/kmol$
 n = pressure exponent of burn rate
[OB] = oxygen balance
 p = pressure, MPa
 q_{cond} = conductive heat flux, kW/m^2
 q_{conv} = convective heat flux, kW/m^2
 q_{reac} = rate of heat production, kW/m^2
 Q = heat release, kJ/kg
 r = burn rate, m/s
 R = gas constant, $8.315 kJ/kmolK$
 T = temperature, K
 u = flow velocity, m/s
 x = distance, m
 Z = pre-exponential factor, $(kg/m^3s)(MPa)^{-\kappa}$
 α = thermal diffusivity, m^2/s
 β = radiative heat flux factor defined in equation 26, kW/m^2K^4
 γ = specific heat ratio
 Γ = heat flux at the burning surface, kW/m^2
 δ = reaction distance, mm
 ΔH_f° = heat of formation, MJ/kg
 λ = thermal conductivity, kW/mK
 Λ = heat flux in the gas phase or in the condensed phase, kW/m^2
 ξ = mass fraction
 π_k = temperature sensitivity of chamber pressure, K^{-1}
 ρ = density, kg/m^3 or g/cm^3
 σ_p = temperature sensitivity of burn rate, K^{-1}
 ϕ = temperature gradient, K/m
 φ = temperature defined in equation 32, K
 ω = reaction rate in the gas phase, kg/m^3s

Subscripts

- c = combustion
- d = decomposition or dark zone
- f = flame or fizz zone
- g = gas phase
- m = melting point
- p = propellant, condensed phase, or product
- r = reactant
- s = burning surface
- 0 = initial condition

1. Introduction

When a propellant is ignited and burned in a closed chamber, gaseous species at high temperature and pressure are formed. These energetic gaseous species generate propulsive forces used for rockets, guns, and fireworks. The specific impulse (I_{sp}) is a parameter used to identify the energy content of propellants and is represented by

$$I_{sp} \sim (T_c/M_c)^{1/2} \quad (1)$$

where T_c is combustion temperature and M_c is molecular weight of the combustion products. Though I_{sp} is also a function of the specific heat ratio (γ) of the combustion products, γ is relatively constant among propellants. It is evident from equation 1 that an energetic material that produces high T_c and high M_c combustion products may not be a useful propellant. A propellant that generates low T_c can also be useful if the M_c is sufficiently low. For example, a pyrolant containing metal powders is not used as a propellant because it generates metallic oxides with a high M_c even though a high T_c is generated by metal combustion.

Solid propellants may be classified into three types by their physical structures: (1) homogeneous propellant, (2) heterogeneous propellant, and (3) granulated propellant. A homogeneous propellant consists of fuel and oxidizer components that are bonded chemically in the same molecule, and the physical structure appears to be homogeneous. A typical example of homogeneous propellant is nitrocellulose (NC) that is composed of $-O-NO_2$ chemical bonds and hydrocarbon structure. Breaking the $O-NO_2$ bond produces NO_2 gaseous species, which act

as an oxidizer fragment, and the hydrocarbon structure acts as a fuel fragment. The physical structure of NC is homogeneous, and it is known as a single-base propellant. The mixture of NC with nitroglycerin (NG) forms a homogeneous gelled propellant known as a double-base propellant. The physical structure of a double-base propellant is also homogeneous.

On the other hand, a heterogeneous propellant is made as a mixture of fuel and oxidizer components, and the physical structure of the propellant is heterogeneous. A typical heterogeneous propellant is a mixture of crystalline particles and a polymeric hydrocarbon, a so-called "composite propellant". The crystalline particles act as the oxidizer component, and the polymeric hydrocarbon acts as a fuel component when these are decomposed. The chemical reaction that produces heat and combustion products occurs on and above the burning surface of the propellant.

A granulated propellant consists of numerous granulated grains or powders that are made from energetic materials. When a granulated propellant is used for a propulsion system, the propellant is a loosely packed shape. Black Powder is a typical example of this class of propellant. However, in some applications (model rocket motors, skyrockets, and signal rockets) Black Powder may be compressed into a single grain and performs as a heterogeneous propellant.

These three types of propellants are fundamentally different from each other in various aspects: chemical ingredients, decomposition processes, burn rate characteristics, combustion products, etc. In this paper the chemical properties of propellants, their ingredients, and combustion characteristics are described in order to understand the ballistic properties of solid propellants.

2. Energetics of Propellants

2.1 Generation of Heat Energy

When a propellant burns, heat and combustion products are produced. In general, the heat produced is evaluated by the “heat of explosion” H_{exp} . H_{exp} is defined as the difference between the heats of formation of the reactants, $\Sigma\Delta H_f^\circ$ (reactants), and the heats of formation of the products, $\Sigma\Delta H_f^\circ$ (products) as represented by

$$H_{exp} = \Sigma\Delta H_f^\circ(\text{reactants}) - \Sigma\Delta H_f^\circ(\text{products}) \quad (2)$$

Each heat of formation, ΔH_f° , is dependent on the chemical structure and chemical bond energy of each molecule of propellant ingredient and combustion products. Equation 2 indicates that a higher H_{exp} is obtained when a higher $\Sigma\Delta H_f^\circ$ (reactants) is used for the propellant and also when a lower $\Sigma\Delta H_f^\circ$ (products) results from the combustion products.

Table 1 shows ΔH_f° for typical energetic reactant ingredients used for propellants, and Table 2 shows ΔH_f° for typical propellant combustion products. It is evident from the data in Table 1 that higher ΔH_f° (reactants) is generally obtained with oxidizers or materials containing nitrogen atoms.

Table 3 shows H_{exp} , percent nitrogen (N%), density (ρ), and melting point temperature (T_m) for typical energetic materials used as major components of propellants. To obtain higher H_{exp} of propellants, various types of chemicals are mixed to formulate propellants. The major chemicals are fuel and oxidizer. The oxidizer oxidizes the fuel to produce heat and gaseous products. Even though $\Sigma\Delta H_f^\circ$ (reactants) of the fuel and oxidizer may be low, a higher H_{exp} is obtained if the oxidizer has a potential to oxidize the fuel completely. The complete oxidation reaction (i.e., complete combustion) produces lower $\Sigma\Delta H_f^\circ$ (products) as the combustion products. Thus, the concentration of oxygen atoms within the oxidizer represented by “oxygen balance: [OB]” is an important parameter to identify the potential of oxidizers. Oxygen balance is the amount of oxygen remaining after oxidizing hydrogen, carbon, magnesium, aluminum, etc. to produce H_2O , CO_2 , MgO , Al_2O_3 , etc. If excess oxygen molecules remain after the oxidation reaction, the oxidizer

Table 1. ΔH_f° for Propellant Reactant Ingredients.

Reactant	ΔH_f° (MJ/kg)
NG	-1.70
NC	-2.60
HMX	+0.25
NH_4ClO_4	-2.52
$KClO_4$	-3.12
NH_4NO_3	-4.56
KNO_3	-4.87
CTPB	-0.89
HTPB	-0.31
GAP	+0.96
BAMO	+2.46
Cubane	+5.47
Al	0
Mg	0
B	0

Table 2. ΔH_f° for Propellant Combustion Products.

Product	ΔH_f° (MJ/kg)
CO	-3.94
CO_2	-8.94
H_2	0
$H_2O_{(g)}$	-13.42
N_2	0
Al_2O_3	-16.4
B_2O_3	-18.30
MgO	-14.93

is termed to have a “positive” oxygen balance. If the oxygen molecules are completely consumed and excess fuel molecules remain, the oxidizer is termed to have a “negative” oxygen balance.

Since the reaction of an oxidizer composed of a $C_aH_bN_cO_dCl_eS_f$ oxidizer is represented by

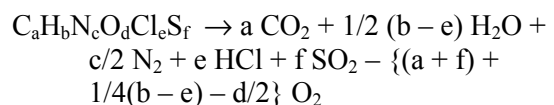


Table 3. Physicochemical Properties of Ingredients Used for Propellants.

Propellant Ingredient	Short-hand	Formula	N (%)	Density (ρ) (g/cm ³)	H_{exp} (MJ/kg)	T_m (°C)	[OB] (%)
nitroglycerine	NG	(ONO ₂) ₃ (CH ₂) ₂ CH	18.50	1.59	6.322	13.2	+3.5
nitrocellulose	NC	C ₁₂ H ₁₄ N ₆ O ₂₂	14.14	1.67	4.13	D	-28.7
ammonium perchlorate	AP	NH ₄ ClO ₄	11.04	1.95	1.114	D	+34.04
ammonium nitrate	AN	NH ₄ NO ₃	35.0	1.72	1.601	169.6	+19.99
nitroguanidine	NQ	CH ₄ N ₄ O ₂	53.83	1.71	2.88	232	-30.7
triaminoguanidine nitrate	TAGN	CH ₉ N ₇ O ₃	58.68	1.5	3.67	216	-33.5
cyclotetramethylene tetranitramine	HMX	(NNO ₂) ₄ (CH ₂) ₄	37.83	1.90	5.36	275	-21.6
cyclotrimethylene trinitramine	RDX	(NNO ₂) ₃ (CH ₂) ₃	37.84	1.82	5.40	204	-21.6
hexanitrohexaazatetradecyclododecane	CL-20	(NNO ₂) ₆ (CH) ₆	38.45	2.04	6.8	260	-10.95

D = decomposes instead of melting.

Note: H_{exp} is for H₂O as a gas.

the oxygen balance, expressed as mass percent, is given by

$$[OB] = - \{ (a + f) + 1/4(b - e) - d/2 \} \times \{ 32 / (\text{molecular mass of oxidizer}) \} \times 100\%$$

For example, NG produces excess oxygen molecules during its combustion as given by



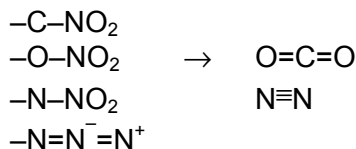
The oxygen balance of NG is given by

$$[OB]_{NG} = \{ + 1/4 \} \times \{ 32 / 227 \} \times 100\% = + 3.52\%$$

The oxygen balance for any type of oxidizer can be obtained by assuming the oxidized products as shown above. Table 3 shows the oxygen balance for some ingredients used in propellants.

2.2 Characterization of Energetic Materials

Typical materials containing oxygen and nitrogen atoms are known as nitrate esters and include nitrocellulose (NC) and nitroglycerin (NG). Nitrate esters consist of -O-NO₂ chemical bonds in their structures. The oxidizer component is oxygen, and the fuel components are carbon and hydrogen. The oxidized combustion products are CO₂ and H₂O_(g) for which ΔH°_f are -8.94 and -13.42 MJ/kg, respectively, as shown in Table 2. The nitrogen atoms in the reactants produce nitrogen gas for which ΔH°_f is zero (Table 2). Also materials containing a -C-NO₂ bond such as trinitrotoluene (TNT: C₇H₅N₃O₆) and tetryl (C₇H₅N₅O₈), those containing a -N-NO₂ bond such as RDX (C₃H₆N₆O₆) and HMX (C₄H₈N₈O₈), and those containing a -N=N=N⁺ bond such as lead azide (Pb(N₃)₂) and glycidyl azide polymer (GAP: C₃H₅N₃O) are high-energy materials useful for propellants. These materials act to produce CO₂ and N₂ through the following combustion reaction



Thus, a high H_{exp} as shown in equation 2 is obtained by the combustion of materials containing these chemical bonds.

Crystalline materials such as KNO_3 , NH_4NO_3 , and NH_4ClO_4 are used as oxidizers due to the high concentration of oxygen atoms in their molecules. These materials generate oxidizing fragments when thermally decomposed. On the other hand, hydrocarbon polymers such as polyurethane and polybutadiene generate gaseous fuel fragments when thermally decomposed. Thus, the mixture of an oxidizer and a hydrocarbon polymer forms a composite propellant. Accordingly, a composite propellant generates high temperature gases during combustion.

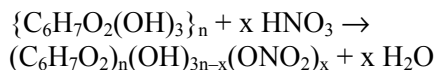
The mechanical properties of propellants are important to produce desirable propellant grains. The mass burn rate of propellant is dependent not only on the linear burn rate of the propellant but also on the burning surface area of the propellant grain. During pressure transient processes, such as ignition and oscillatory burning in a rocket motor, very high mechanical stresses are produced in the propellant grain. If the internal grain shape is complicated, these stresses may damage the propellant grain. The increased burning surface area caused by unexpected damage, such as cracks, to the grain increases pressure in the combustion chamber. Furthermore, the elongation property (elasticity) decreases as the temperature decreases. This may cause damage to the grain when mechanical shock is applied to the grain at low temperature. On the other hand, mechanical strength decreases as temperature increases. This may allow deformation of the grain due to its mass. Accordingly, the propellant grain geometry should be maintained by adequate elongation and strength properties of the propellant.

3. Propellant Ingredients

3.1 Homogeneous Propellants

Nitrocellulose (NC) is a major energetic ingredient used for single-base and double-base propellants. As shown in Table 3, NC is a nitrate ester composed of carbon, hydrogen, oxygen, and nitrogen atoms. The oxygen atoms are attached as $-\text{O}-\text{NO}_2$ with a nitrogen atom. When NC is thermally heated, NO_2 is formed because the $\text{O}-\text{N}$ bond is the weakest of the NC chemical bonds. The remaining oxygen then forms aldehydes such as HCHO and CH_3CHO . The reaction between NO_2 and aldehydes produces heat and the combustion gases that are used for propulsive forces in rockets, guns, and pyrotechnics.

In general, NC is produced from the cellulose, $\{\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3\}_n$, of cotton or wood, which is nitrated using nitric acid (HNO_3) to gain $-\text{O}-\text{NO}_2$ bonds in its structure as



Through this nitration the $-\text{OH}$ contained within the cellulose is replaced with $-\text{O}-\text{NO}_2$; the degree of nitration determines the energy available to form high temperature combustion gases. The maximum nitration is obtained when the nitrogen mass becomes 14.14% within NC.

The major ingredient of single-base propellant is NC. Diphenylamine, $(\text{C}_6\text{H}_5)_2\text{NH}$, is also added as a chemical stabilizer. In some cases, a small amount of K_2SO_4 or KNO_3 is mixed as a flame-suppressor. Ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) or diethylether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$) is mixed within the NC to soften it and to gain an adequate size and shape of the propellant grain. The grain surface is coated with carbon black to keep the surface smooth.

A double-base propellant is also known as smokeless powder [propellant] when used for guns and rockets. Two major ingredients are used to formulate double-base propellant grains: NC and nitroglycerin (NG). NG, $\text{C}_3\text{H}_5(\text{ONO}_2)_3$, is also a nitrate ester characterized with the $-\text{O}-\text{NO}_2$ structure and is a high explosive. Since NG is liquid at room temperature, NG is absorbed by the NC and acts to gelatinize NC to form double-base propellant grains.

Table 4. Physicochemical Properties of Nitrate Esters Used for Double-base Propellants.

Nitrate Ester	N (%)	Density (ρ) (g/cm ³)	ΔH_f° (r) (MJ/kg)	H_{exp} (MJ/kg)	T_m (°C)	[OB] (%)
diethyleneglycol dinitrate (DEGDN) (CH ₂) ₄ O(ONO ₂) ₂	14.29	1.38	-2.208	4.852	2	-40.8
triethyleneglycol dinitrate (TEGDN) (CH ₂) ₆ O ₂ (ONO ₂) ₂	11.67	1.34	-2.526	3.140	-19	-66.7
trimethylolethane trinitrate (TMETN) CH ₃ C(CH ₂) ₃ (ONO ₂) ₃	16.46	1.47	-1.610	5.527	-3	-34.5

Since NG is highly shock sensitive, other types of nitrate esters can be used to formulate non-NG double-base propellants. Diethyleneglycol dinitrate (DEGDN), (CH₂)₄O(ONO₂)₂, triethyleneglycol dinitrate (TEGDN), (CH₂)₆O₂(ONO₂)₂, and trimethylolethane trinitrate (TMETN), CH₃C(CH₂)₃(ONO₂)₃ are typical examples of energetic nitrate esters that are mixed with NC. Though these nitrate esters are less energetic than NG, the required mass fraction of desensitizers required is less for the nitrate esters than it is for NC/NG double-base propellants. The physicochemical properties of these nitrate esters are shown in Table 4.

Two production methods are used to produce double-base propellant grains: (1) extrusion using an external mechanical press and (2) casting using finely divided NC powders or NC/NG powders. The extrusion method is used for grains less than 0.1 kg, typically used in guns and pyrotechnics. The casting method is used for grains larger than 1 kg such as rockets. Since NG is a detonative explosive, the concentration of NG is kept approximately less than $\xi(0.5)$ for double-base propellants. Furthermore, various chemicals such as plasticizers, stabilizers, and burn rate modifiers are added to NC/NG mixtures to improve the physicochemical properties of double-base propellants.

The mechanical properties and shock sensitivities of double-base propellants are highly dependent on the mixture ratio of NC and NG. Though the specific impulse of double-base propellants increases with the concentration of NG, the strength of the propellant decreases. It becomes difficult to maintain grain shape when the concentration of NG is as high as $\xi(0.5)$. For example, dynamites contain more than $\xi(0.8)$ NG, and their grains are very soft and have high shock sensitivity. When the concentration of NC becomes higher than $\xi(0.6)$, the elongation properties become poor. Thus, double-base propellants need to contain desensitizers, stabilizers, and chemicals to improve mechanical properties. In order to obtain superior mechanical properties, plasticizers such as dibutylphthalate (DBP), C₁₆H₂₂O₄; diethylphthalate (DEP), C₁₂H₁₄O₄; triacetin (TA), C₉H₁₄O₆; and stabilizers such as ethyl centralite (EC), CO{N(C₆H₅)(C₂H₅)}₂ are added. Table 5 shows the physicochemical properties of the plasticizers and stabilizers used for double-base propellants. These chemicals are used to obtain superior grain formation and to improve mechanical properties, shock sensitiveness and chemical stability.

Table 5. Plasticizers and Stabilizers Used for Double-base Propellants.

Plasticizers and Stabilizers	N (%)	Density (ρ) (g/cm ³)	ΔH_f° (r) (MJ/kg)	[OB] (%)
dibutylphthalate (DBP) C ₁₆ H ₂₂ O ₄	0	1.045	-3.027	-224.2
triacetin (TA) C ₉ H ₁₄ O ₆	0	1.15	-5.606	-139.4

Table 6. Ingredients Used for Double-Base Propellants.

Plasticizer (Oxidizer and Fuel)		Plasticizer (Energetic Fuel)	
NG	nitroglycerin	GAP	glycidylazido polymer
TMETN	trimethylolethane trinitrate	BAMO	bis-azide methyloxetane
TEGDN	triethyleneglycol dinitrate	AMMO	3-azidomethyl-3-methyloxetane
DEGDN	diethyleneglycol dinitrate		
DNT	dinitrotoluene		
Plasticizer (Fuel)		Binder (Fuel and Oxidizer)	
DEP	diethylphthalate	NC	nitrocellulose
DBP	dibutylphthalate		
TA	triacetine		
PU	polyurethane		
Burn Rate Catalyst		Stabilizer	
PbSa	lead salicylate	EC	ethyl centralite
PbSt	lead stearate	2NDPA	2-nitrodiphenylamine
Pb2EH	lead 2-ethylhexanoate	DPA	diphenylamine
CuSa	copper salicylate		
CuSt	copper stearate		
LiF	lithium fluoride		
High Energy Additive (CMDB Propellant)		Burn Rate Catalyst Modifier	
RDX	cyclotrimethylene trinitramine	C	carbon black (used with lead or copper salts)
NQ	nitroguanidine		
HMX	cyclotetramethylene tetranitramine		
CL-20	hexanitrohexaazatetracyclodecane		
ADN	ammonium dinitramide		
Combustion Instability Suppressant		Oxidizer (CMDB Propellant)	
Al	aluminum	AP	ammonium perchlorate
Zr	zirconium	HNF	hydrazinium nitroformate
ZrC	zirconium carbide		
		Coolant (Fuel)	
		OXM	oxamide
		TAGN	triaminoguanidine nitrate
		Opacifier	
		C	carbon black
		Metal Fuel	
		Al	aluminum

The I_{sp} and T_f (T_f is the adiabatic flame temperature) of double-base propellants are dependent on the mass fraction of NG, $\xi(\text{NG})$, mixed within the NC and other chemicals. When a double-base propellant is composed of NG, NC, and DEP (the additional mass fraction of DEP is 0.10), the maximum I_{sp} and T_f are obtained at $\xi(\text{NG}) = 1.0$ as shown in Figure 1. It should be noted that the I_{sp} and T_f of the double-

base propellants composed of NC and NG without plasticizers and stabilizers are maximized at $\xi(\text{NG}) = 0.75$.

Table 6 shows materials used to formulate double-base propellants. Typical examples of chemical compositions and energetics of double-base propellants are shown in Table 7.

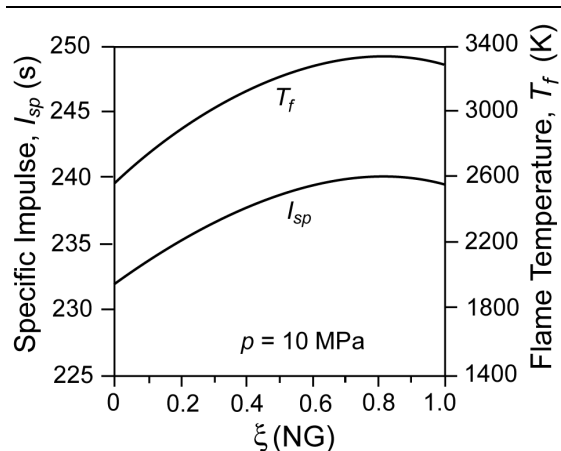
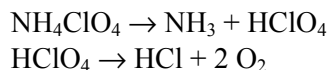


Figure 1. Combustion performance of double-base propellant as a function of NG (the propellant contains an additional mass fraction of 0.1 DEP).

3.2 Heterogeneous Propellants

When crystalline oxidizer particles are mixed with a hydrocarbon polymer, a heterogeneous propellant, or “composite propellant”, is formed. Unlike double-base propellants, the physical structure of composite propellants is heterogeneous due to the dispersed crystalline particles within the polymer. As described previously, at the burning surface of the propellant, the oxidizer particles generate gaseous oxidizing fragments, and the polymer generates gaseous fuel fragments. Both gaseous fragments diffuse with each other and react to generate heat and combustion products. Accordingly, ballistic properties, such as burn rate and pressure sensitivity, are dependent not only on the chemical properties of oxidizers and binders but also are dependent on the shape and size of the oxidizer particles.

The major oxidizer used for composite propellants is ammonium perchlorate (AP), NH_4ClO_4 . When AP is heated, it decomposes as



The oxidizing fragments react with fuel fragments when these crystalline materials are mixed with fuel components, for example,

Table 7. Chemical Compositions and Energetics of Typical Double-Base Propellants.

NC	NG	DEP	2NDPA	T_f (K)	H_{exp} (MJ/kg)
53.0	40.5	4.0	2.5	2800	4.62
48.0	36.7	13.0	2.3	2200	3.78



This reaction produces significant heat and gaseous molecules, which yields a high I_{sp} as defined in equation 1.

Ammonium nitrate (AN), NH_4NO_3 , is a halogen-free oxidizer, which produces nontoxic combustion products. However, disadvantages of AN compared with AP are hygroscopicity and crystal structure transitions at 125.2, 84.2, 32.3, and -16.9 °C. These transitions produce internal mechanical stresses in the propellant grain, which sometimes damages the grain. Though potassium nitrate (PN), KNO_3 , and potassium perchlorate (PP), KClO_4 , produce high temperature combustion products, the combustion products contain potassium oxide (K_2O), which has high M_c and significantly reduced I_{sp} . PN is a well-known oxidizer used as the oxidizer in Black Powder. PP is also used as an oxidizer in pyrotechnic compositions.

The binders, used to adhere oxidizer particles to form propellant grains, are also fuel ingredients. Table 8 shows typical polymers used for composite propellants.

The binders are based on hydrocarbon polymers that have a relatively low viscosity during the process of mixing the oxidizer particles and the polymer before the curing process. Two types of polymers are commonly used for modern propellants: (1) polyurethane copolymer and (2) polybutadiene copolymer. Polyether and polyester types of polyurethane copolymers are used. The molecular concentration of hydrogen contained within polybutadiene copolymers is relatively high, and the heat of formation is also high. Also, the viscosity of the copolymer is low enough to allow mixing with oxidizer particles before curing.

Table 8. Type of Polymers Used for Composite Propellants.

Polymeric Binder	Basic Polymer Unit
Polyethylene	$-\text{CH}_2-\text{CH}_2-$
Polyester	$-(\text{CH}_2)-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$
Polyurethane	$-\text{O}-(\text{CH}_2)_n-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-(\text{CH}_2)_n-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-$
Polybutadiene	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$

Polybutadiene-acrylonitrile (PBAN) is used as the binder in the booster propellant of the Space Shuttle. Carboxy-terminated polybutadiene (CTPB) and hydroxy-terminated polybutadiene (HTPB) are used widely for modern composite propellants. CTPB and HTPB form regularly distributed matrices of polymers through crosslinking reactions. For example, HTPB polymer, $\text{HO}-(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n-\text{OH}$, is cured using isophorone diisocyanate (IPDI) to form a polymeric binder. Using this binder, it is possible to achieve a high loading percentage of oxidizer. To gain superior mechanical properties a small amount of bonding

agent is added to adhere each oxidizer particle to the binder. As shown in Figure 2a, the maximum I_{sp} , 259 s, ($p = 10$ MPa), is obtained when the mass fraction of AP, $\xi(\text{AP})$, is 0.89 mixed with a mass fraction of HTPB binder of 0.11.

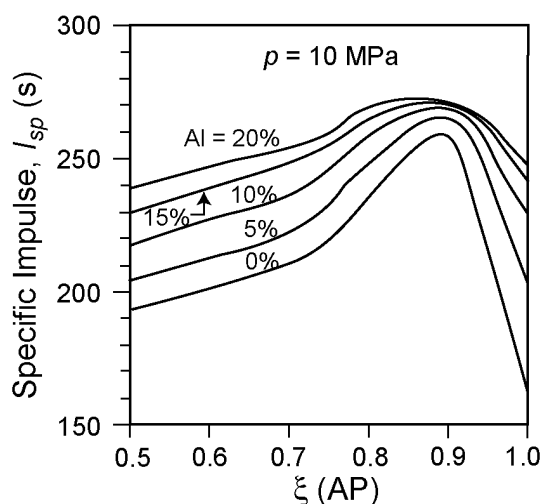


Figure 2a. Specific impulse of AP/HTPB/Al propellant as a function of the mass fraction of AP.

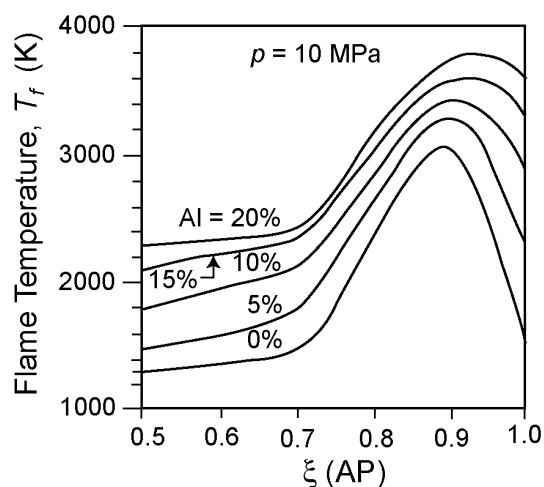


Figure 2b. Adiabatic flame temperature of AP/HTPB/Al as a function of the mass fraction of AP.

To gain higher I_{sp} with AP-based composite propellants, aluminum particles are added as a fuel component. Though the addition of aluminum particles increases the M_c , the increase of T_f is the larger effect resulting in higher I_{sp} . The effect of aluminum addition on the adiabatic flame temperature is shown in Figure 2b. However, it should be noted that the maximum solid fraction within composite propellants is limited to approximately 0.85 due to mixing difficulties.

When aluminum particles are added to composite propellants, white smoke is generated due to the combustion product, aluminum oxide. If the smoke is not desirable because of military requirements or use in a fireworks display, aluminum particles cannot be used. Furthermore, if the atmosphere is very humid, white smoke is also generated due to the HCl – produced as a combustion product. This is because the HCl molecule acts as a nucleus for moisture from the atmosphere, and relatively large-sized water drops are formed producing a fog or a mist. This occurs only when the humidity in the atmosphere is high or the temperature is low (below $-10\text{ }^\circ\text{C}$). Double-base propellants are classified as smokeless propellants, and composite propellants, using AN as an oxidizer without halogen molecules, are also known as smokeless propellants.

Since composite propellants consist of crystalline particles and polymeric binders, the mechanical properties of propellant grains are dependent on the physical and chemical properties of these ingredients and also of the additives such as bonding agents, surfactants, crosslinkers, and curing agents. The binder, as well as the mass fraction and particle size of the oxidizer, determine the characteristics of mechanical strength and elongation.

The polymers chosen for composite propellants are dependent on application conditions. Low viscosity is needed to allow high concentrations of AP particles, aluminum powders, and metallic powders used for burn rate modifiers, to achieve high I_{sp} . HTPB is considered to be the best binder to obtain both high combustion performance and superior elongation properties at low temperatures. HTPB is characterized with $-\text{OH}$ terminal of butadiene polymer. Another useful butadiene polymer is carboxy-

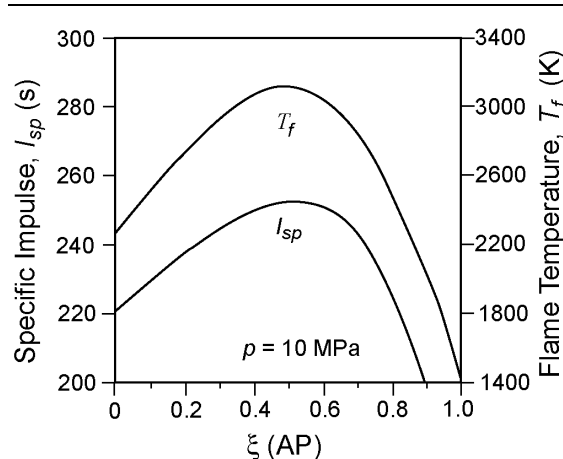


Figure 3. Combustion performance of AP-CMDB propellant as a function of the mass fraction of AP.

terminated polybutadiene (CTPB). The prepolymer of HTPB is cured and crosslinked using isophorone diisocyanate (IPDI) to form HTPB polymer, useful as a binder. The functionality of the HTPB prepolymer is also an important chemical parameter during the process of curing and crosslinking to achieve superior mechanical properties of the HTPB binder.

The propellant composed of AP particles with NC/NG used as a binder is the so-called “ammonium perchlorate based composite modified double-base propellant (AP-CMDB propellant)”. AP-CMDB propellant is called a composite propellant because of its physical structure. However, the binder of NC/NG burns by itself and produces numerous diffusional flamelets around each AP particle at the burning surface. The AP particles act as an oxidizer to increase T_f and I_{sp} . Figure 3 shows the T_f and I_{sp} of AP-CMDB propellants at $p = 10\text{ MPa}$ as a function of $\xi(\text{AP})$. The base matrix used as a binder is composed of NC/NG = 1/1. The maximum T_f and I_{sp} are obtained at $\xi(\text{AP}) = 0.5$.

Table 9 shows the materials used to formulate composite propellants. An example of the chemical composition of a composite propellant is shown in Table 10.

Table 9. Chemical Ingredients Used for Composite Propellants.

Oxidizer		Binder (Fuel)	
AP	ammonium perchlorate	HTPB	hydroxy-terminated polybutadiene
AN	ammonium nitrate	CTPB	carboxy-terminated polybutadiene
HNF	hydrazinium nitroformate	PU	polyurethane
		PS	polysulfide
		PVC	polyvinyl chloride
Curing and/or Crosslinking Agent		Binder (Energetic Fuel)	
IPDI	isophorone diisocyanate	GAP	glycidylazido polymer
TDI	toluene-2,4-diisocyanate	BAMO	bis-azidemethyloxetane
PQD	paraquinone dioxime	AMMO	3-azidomethyl-3-methyloxetane
HMDI	hexamethylene diisocyanate		
MAPO	tris(1-(2-methyl)aziridinyl) phosphine oxide		
		Bonding Agent	
Metal Fuel		MAPO	tris(1-(2-methyl)aziridinyl) phosphine oxide
Al	aluminum	TEA	triethanolamine
		MT-4	adduct of 2.0 moles MAPO, 0.7 mole adipic acid, and 0.3 mole tartaric acid
Plasticizer		Burn Rate Catalyst	
DOA	dioctyl adipate	Fe ₂ O ₃	ferric oxide
IDP	isodecyl pelargonate	FeO(OH)	hydrated ferric oxide
DOP	dioctylphthalate	NBF	n-butyl ferrocene
		LiF	lithium fluoride
High Energy Additive		HCl Suppressant	
RDX	cyclotrimethylenetrinitramine	Mg	magnesium
HMX	cyclotetramethylenetetranitramine	MgAl	magnalium
NQ	nitroguanidine	NaNO ₃	sodium nitrate
CL-20	hexanitrohexaazatetracyclo- dodecane		
ADN	ammonium dinitramide		
Combustion Instability Suppressant			
Al	aluminum		
Zr	zirconium		
ZrC	zirconium carbide		

3.3 Granulated Propellants

Granulated propellants are used in a loosely packed shape containing numerous individual grains or powders. Though single-base propellants normally are classified as homogeneous propellants, some propulsion applications use a

packed shape consisting of granulated single-base propellant.

Black Powder is a typical granulated propellant used for propulsion and is used as a propellant for small-sized rockets, guns, and fireworks. Though the theoretical I_{sp} of Black Powder is less than that of single-base, double-base, and

Table 10. Chemical Composition and Combustion Products of a Typical Composite Propellant.

Ingredients (weight %)		T_f , K	Products (mole fractions)					
AP	HTPB		CO	CO ₂	HCl	H ₂ O	N ₂	H ₂
80.0	20.0	2358	0.251	0.055	0.143	0.244	0.075	0.213

AP-based composite propellants, Black Powder is useful for short-duration operations of simplified propulsive systems. The advantages of Black Powder are low cost, very low aging effect, and simple adjustment of propulsive forces by the amount used.

Black Powder is a mechanically mixed material of PN powder (60–80%), charcoal (10–25%), and sulfur (8–25%) that is pressed, granulated, and formed as a packed shape for use. When Black Powder is ignited, combustion occurs over all granulated surfaces. Thus, the rate of gas production becomes much higher than that of conventional propellants used for rockets. However, this combustion phenomenon is deflagration, not detonation. The burn rate of Black Powder is not defined as that of rocket propellants because of the nature of the granulated combustion, except when pressed in some applications. The overall gas production rate is an important combustion parameter, and it is dependent on the granulation size of the powder as well as the density of the packed shape. The specific impulse, I_{sp} , ranges from 60 to 150 s, and the combustion temperature ranges from 1400 to 3200 K. These values are determined by the mixture ratio of the ingredients.

In general, powdered grains made of single-base, double-base, and triple-base propellants are classified as granulated propellants. These are used as gun propellants, and the burn time is on the order of 10 to 100 ms. The mass burn rate of these grains is very high because the web thickness is very thin compared to rocket propellants, and the burning pressure is on the order of 100 to 1000 MPa. Though the physical structures of single-base and double-base granulated grains are essentially homogeneous, these grains burn independently in combustion chambers. Thus, the flame structures appear to be heterogeneous in nature. The shape of each grain is designed to obtain the desired pressure versus time relationship during burning. The reaction products of granulated propellants are essentially the same as Black Powder, single-base gun propellant, or double-base rocket propellant. Table 11 shows the chemical composition of a typical single-base propellant. Table 12 shows the chemical composition and properties of typical Black Powder.

Table 11. Chemical Composition and Combustion Products of a Typical Granulated Single-base Propellant.

Ingredients (weight %)				T_f , K	Products (moles/kg)				
NC	DNT	DBP	DPA		CO ₂	CO	H ₂ O	H ₂	N ₂
85.0	10.0	5.0	1.0	1598	2.32	22.84	5.81	9.55	4.39

Table 12. Chemical Compositions and Properties of Typical Black Powders.

Ingredient	Percentage
potassium nitrate	60 – 80
charcoal	10 – 25
sulfur	8 – 25

Property	Range of Values
I_{sp} , s	60 – 150
Density, g/cm ³	1.2 – 2.0
Flame temperature, K	1400 – 3200

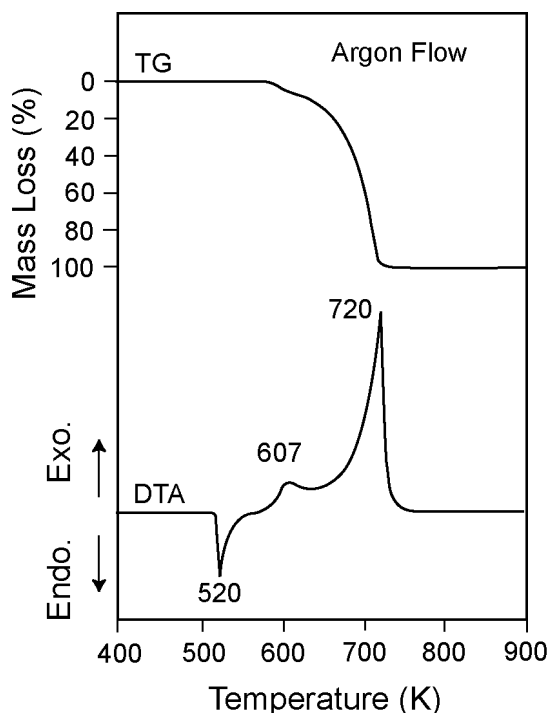


Figure 4. Thermochemical data of AP obtained by DTA and TG showing an endothermic peak at 520 K and an exothermic peak at 720 K.

4. Reaction of Propellants

4.1 Thermal Decomposition Process

There have been numerous studies on the decomposition of propellants and their ingredients to elucidate the aging mechanisms and burn rate characteristics. Various types of experimental techniques are used: (1) differential thermal analysis (DTA), (2) thermogravimetric analysis (TG), (3) Fourier transform infrared analysis (FTIR), (4) Raman spectrum (RS), (5) gas chromatography (GC), and (6) scanning electron microscopy (SEM). Since the chemical process of aging is very slow and the decomposition process for combustion is very fast, the experimental techniques shown above are applied at accelerated conditions for aging analysis and at decelerated conditions for combustion process analysis.

Typical examples of the thermal decomposition process of AP as obtained by DTA and TG are shown in Figure 4. These experiments are conducted to determine the endothermicity

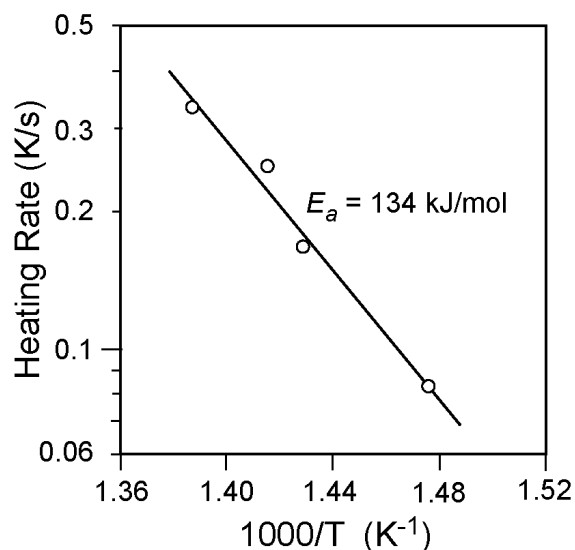


Figure 5. Arrhenius plot of reciprocal exothermic peak temperature as a function of heating rate obtained by DTA.

and/or exothermicity of AP decomposition. The AP sample size was 5 mg in a quartz cell under an argon atmosphere. The heating rate is varied from test to test and ranged from 0.08 to 0.33 K/s. An endothermic peak is seen at 520 K, and an exothermic peak temperature is seen at 720 K using a heating rate 0.33 K/s.

When the heating rate is increased, these peaks shift toward higher temperatures. As shown in Figure 5, the plot of reciprocal temperature versus heating rate produces a straight line that determines the activation energy of the observed phenomenon. Based on data at different heating rates, the activation energy E_a for the decomposition is determined to be 134 kJ/mol. The activation energy of the burning surface decomposition is used to determine burn rate characteristics at high-pressure conditions.

4.2 Characteristics of Thermal Decomposition

The thermal decomposition process is different for each material. For example, the exothermicity of NG is different from that of NC even though both are nitrate esters. Also, the exothermicity of a double-base propellant that is a mixture of NG and NC appears to be different from that of either NG or NC and is also different from an averaged value of NG and

NC. This indicates that the thermal decomposition property of propellant is not an averaged value of each propellant ingredient. Furthermore, the exothermicity of an AP-based composite propellant is much higher than the sum of the exothermicity of each ingredient because an exothermic oxidation reaction occurs between AP and binder.

Though the aging chemistry of propellants is complicated, the surface chemistry between oxidizer particles and binder plays a dominant role in determining the aging period. No definite methods are available to quantify such a very slow reaction mechanism, however, one can estimate it through theoretical analysis based on the data from DTA, TG, and other thermal measurement equipment.

The thermal decomposition at the burning surface of a propellant is more than 10^4 times higher than that of DTA and TG heating rates. Though the data obtained by DTA and TG cannot be applied to determine ballistic characteristics, these are used to determine the thermal properties of propellant burning.

5. Propellant Combustion

5.1 Stable Combustion of Rocket Motor

The thrust of a rocket motor is expressed by

$$F = c_f A_t p_c \quad (3)$$

where F is thrust, p_c is pressure in the combustion chamber of the rocket motor, A_t is the nozzle throat area, and c_f is the dimensionless thrust coefficient, which is determined by the nozzle expansion ratio of the rocket motor, the specific heat ratio, and the atmospheric and chamber pressures.

The mass generation rate in the combustion chamber, m_g , is given by

$$m_g = \rho_p A_b r \quad (4)$$

where r is burn rate of the propellant, A_b is the burning surface area of the propellant, and ρ_p is the density of the propellant. The mass discharge rate from the nozzle, m_d , is then given by

$$m_d = c_d A_t p_c \quad (5)$$

where c_d is the nozzle discharge coefficient that is determined by the combustion properties of propellant such as combustion temperature, molecular mass and specific heat ratio of the combustion products.

The mass balance of the rocket motor at steady-state is given by

$$m_g = m_d \quad (6)$$

From equations 4, 5 and 6, the chamber pressure is determined to be

$$p_c = \rho_p K_n r / c_d \quad (7)$$

where $K_n = A_b / A_t$, which is determined by the physical dimensions of the rocket motor design. In general, the burn rate of the propellant increases linearly as the pressure increases in a $\ln p$ versus $\ln r$ plot at constant initial temperature T_0 , where r is the burn rate and p is the pressure. Thus, the burn rate is represented by the experimental law, Vieille's law or Saint Robert's law, as

$$r = ap^n \quad (8)$$

where n is the pressure exponent of the burn rate and a is constant at constant initial propellant temperature T_0 . Substituting equation 8 into equation 7, one obtains

$$p_c = (a \rho_p K_n / c_d)^{1/(1-n)} \quad (9)$$

The mass balance of a rocket motor is illustrated in Figure 6.

5.2 Burn Rate Characteristics

The pressure sensitivity of the burn rate is expressed as

$$n = d(\ln r) / d(\ln p) \quad \text{at constant } T_0 \quad (10)$$

The burn rate increases also as T_0 increases at constant pressure. A typical example of the results obtained by a strand burner at $T_0 = 233$ and 333 K is shown in Figure 7, which is a $\log p$ vs $\log r$ plot. The temperature sensitivity of burn rate, σ_p , is defined as the fraction of burn rate increase per K as when the initial propellant temperature is increased at constant pressure

$$\sigma_p = (r_1 - r_0) / \{(T_1 - T_0)r\} \quad (11)$$

where r_0 and r_1 are the burn rates at temperatures T_0 and T_1 , respectively. The differential form of σ_p is

$$\sigma_p = d(\ln r) / dT_0 \quad \text{at constant } p \quad (12)$$

Substituting equation 8 into equation 12, one gets

$$\sigma_p = d(\ln(ap^n)) / dT_0 = (da/dT_0) / a \quad \text{at constant } p \quad (13)$$

When T_0 of the propellant in the combustion chamber is changed, p_c is changed according to the relationship of equation 7. The temperature sensitivity of the chamber pressure π_k is defined as

$$\pi_k = (p_{c1} - p_{c0}) / \{(T_1 - T_0)p_c\} \quad \text{at constant } K_n \quad (14)$$

where p_{c0} and p_{c1} are the chamber pressures at T_0 and T_1 , respectively. The differential form of equation 14 is given by

$$\pi_k = d(\ln p_c) / dT_0 \quad \text{at constant } K_n \quad (15)$$

Substituting equation 9 into equation 15, one obtains

$$\pi_k = (da/dT_0) / a(1-n) = \sigma_p / (1-n) \quad (16)$$

Thus, it should be noted that the initial propellant temperature, T_0 , and the pressure exponent of the burn rate n are important parameters in determining the chamber pressure p_c (i.e., thrust

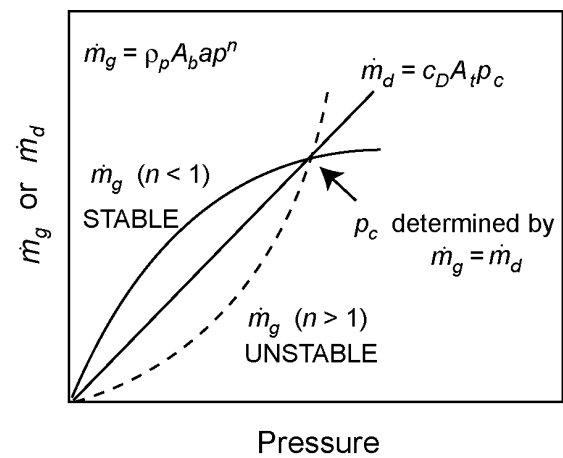


Figure 6. Mass balance of the mass generation in chamber and the mass discharge from nozzle showing the conditions of stable and unstable burning.

of the rocket motor) as shown by equation 3 at different initial propellant temperatures. Figure 8 shows a typical result of rocket-motor firing tests at $T_0 = 233$ and 333 K (constant K_n). The propellant used is an HTPB/AP composite propellant composed of $\xi(\text{AP}) = 0.84$ with $\sigma_p = 0.003/\text{K}$ and $n = 0.5$ ($\pi_k = 0.006/\text{K}$). It is important to note that the chamber pressure increased from 4.9 MPa ($T_0 = 233$ K) to 8.0 MPa ($T_0 = 333$ K).

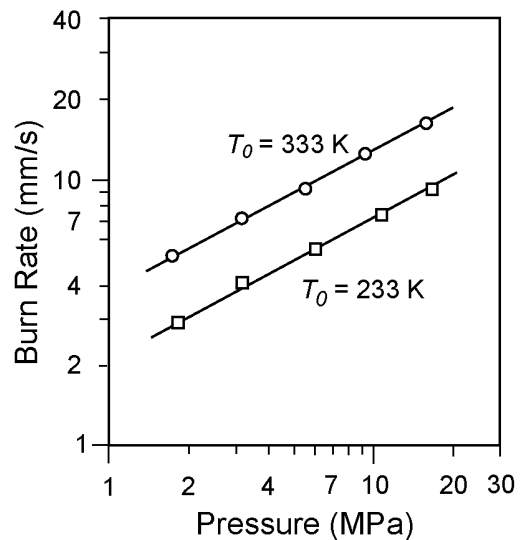


Figure 7. Burn rate versus pressure at different initial-propellant temperatures.

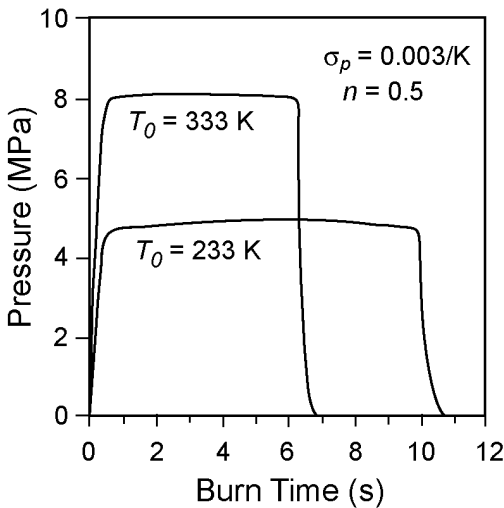


Figure 8. Firing test results of a rocket motor at different temperatures.

5.3 Combustion Wave Structure of Propellants

The burn rate of solid propellant is dependent on various physicochemical parameters such as propellant chemical ingredients, particle size of crystalline oxidizers, chamber pressure, initial propellant temperature, and burn rate catalysts. A schematic representation of the combustion wave of a solid propellant is shown in Figure 9a. In the condensed phase zone (zone I), no chemical reactions occur, and the temperature increases from the initial temperature (T_0) to the decomposition temperature (T_d). In the solid phase reaction zone (zone II), the temperature increases from T_d to the burning surface temperature (T_s), where a phase change from solid to liquid and/or to gas occurs, and reactive gaseous species are formed. In the gas phase reaction zone (zone III), the temperature increases rapidly from T_s to the flame temperature (T_f), where an exothermic gas phase reaction takes place.

During steady state burning of a propellant, the heat transfer in the combustion wave occurs as illustrated in Figure 9b. The energy conservation equation in the combustion wave is represented by

$$q_{cond}(x) + q_{conv}(x) + q_{reac}(x) = 0 \quad (17)$$

where

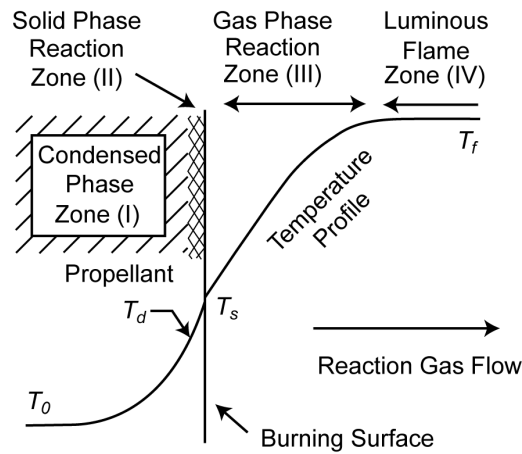


Figure 9a. Thermochemical structure of combustion wave of a solid propellant.

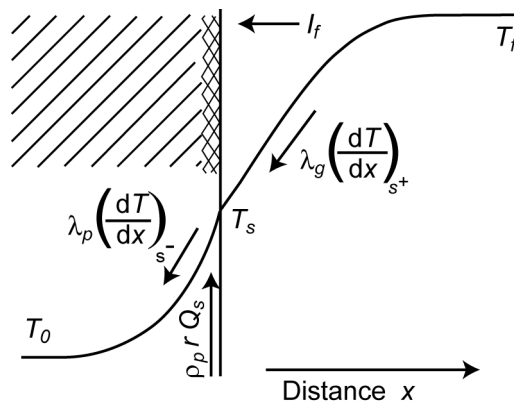


Figure 9b. Heat balance in combustion wave of a solid propellant.

$$q_{cond}(x) = \lambda_g d\phi/dx \quad (18)$$

$$q_{conv}(x) = -mc_g\phi \quad (19)$$

$$q_{reac}(x) = Q_g\omega_g(x) \quad (20)$$

If one assumes that physical properties λ_g and c_g are constant in the gas phase, equation 17 is represented by

$$\lambda_g d\phi/dx - \rho_p rc_g\phi + Q_g\omega_g(x) = 0 \quad (21)$$

where the mass conservation-equation is represented by

$$m = \rho_g u_g = \rho_p r \quad (22)$$

The over-all reaction rate in the gas phase can be represented by

$$\omega_g \delta = \int \omega_g(x) dx = m \quad (23)$$

At the burning surface, the heat flux feedback from the gas phase reaction (zone III) to the burning surface (zone II) by conductive heat transfer is given by

$$\Lambda_g = \lambda_g \phi \quad (24)$$

where ϕ is the temperature gradient in zone III at the burning surface represented by

$$\phi = (dT/dx)_{s,III} \quad (25)$$

The heat flux feedback from zone III to zone II by radiative heat transfer is given by

$$I_f = \beta T^4 \quad (26)$$

The heat flux produced in zone II is given by

$$\Gamma_s = \rho_p r Q_s \quad (27)$$

The heat flux feedback from the burning surface to the condensed phase (zone I) is given by

$$\Lambda_p = \rho_p c_p (T_s - T_0) \quad (28)$$

The overall heat balance at the gas/condensed phase interface is represented by

$$\Lambda_p = \Lambda_g + I_f + \Gamma_s \quad (29)$$

The determination of the magnitude of each term of equation 29 is the center of research on the combustion study of energetic materials.

If one assumes that the radiative heat flux feedback from zone III to zone II is much smaller than the other terms, the burn rate is obtained by substituting equations 24, 27 and 28 into equation 29 and then solving for r

$$r = \alpha_s \phi / \varphi \quad (30)$$

where

$$\alpha_s = \lambda_g / \rho_p c_p \quad (31)$$

$$\varphi = T_s - T_0 - Q_s / c_p \quad (32)$$

Equation 30 indicates that the burn rate of solid propellants is determined by two parameters: the gas phase parameter ϕ , which is determined by the physical and chemical properties in the gas phase, and the condensed phase pa-

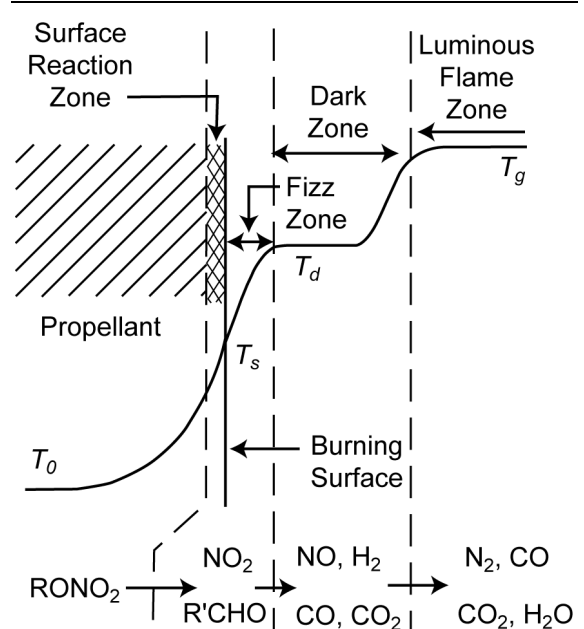


Figure 10. Combustion wave structure of a double-base propellant.

rameter φ , which is determined by the physical and chemical properties in the condensed phase.

5.4 Combustion of Homogeneous Propellant

The combustion wave of a homogeneous propellant is known to consist of successive one-dimensional, homogeneous reaction zones. Figure 10 shows a typical example of the combustion wave of double-base propellants. There exist four reaction zones: surface, fizz, dark, and flame zones. The temperature increases smoothly from the initial propellant temperature T_0 to the burning surface temperature T_s , to the dark zone temperature T_d , and to the flame zone temperature T_g .

At the surface reaction zone (including sub-surface reaction), NO_2 is formed due to the breaking of O-NO_2 bonds in the nitro groups of NC and NG. The decomposition of the remaining fragments follows, producing fuel components such as aldehydes. These combustible gaseous species react rapidly in the fizz zone and produce large amounts of heat. Thus, a steep temperature rise is observed in the fizz zone. In the succeeding dark zone, the NO produced by the reduction of NO_2 in the fizz zone reacts slowly, and the temperature also rises slowly. The NO and the rest of the fuel prod-

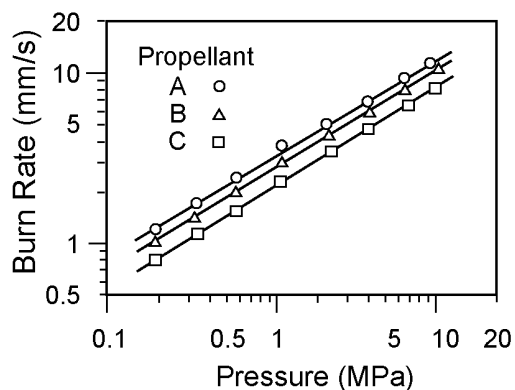


Figure 11. Burn rate of double-base propellants as a function of pressure showing that the pressure exponent remains unchanged when the mixture ratio of NC/NG is changed.

ucts react more rapidly after some elevated temperature is achieved at some distance from the burning surface and form the luminous flame zone. In this flame zone, the final combustion products, such as N_2 , CO_2 , H_2O , etc., are produced, and the temperature reaches its maximum. These reaction processes are largely dependent on pressure.

The burn rate of a double-base propellant is approximately a straight line in a $\log p$ versus $\log r$ plot. As shown in Figure 11, the pressure exponent is unchanged when the mixture ratio of NC/NG is changed. Table 13 shows the chemical compositions of double-base propellants—A, B, and C. The pressure exponent, n , of the burn rate is determined to be 0.60.

The photographic observation of the flame structure shows that the luminous flame zone approaches the burning surface as the pressure increases. The dark zone length, which is approximately equal to the luminous flame stand-off distance, L_d , (the fizz zone length is much shorter than that of the dark zone length), is

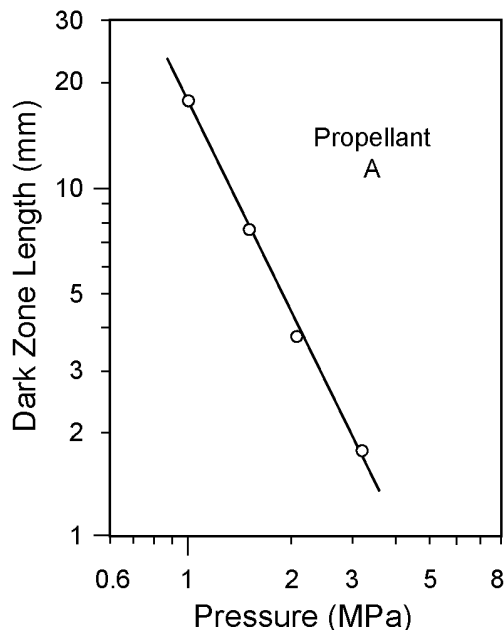


Figure 12. Dark zone length versus pressure for a double-base propellant A.

represented by

$$L_d = ap^d = ap^{n-m} \quad (33)$$

where d is the dark-zone pressure exponent, m is the overall reaction order in the dark zone, n is the pressure exponent of the burn rate, and a is a constant. From the data shown in Figure 12, d is determined to be -2.0 . The overall reaction order in the dark zone is determined to be approximately 2.6. This reaction order indicates that the reaction in the dark zone is more pressure sensitive than other gas-phase reactions of which reaction orders are approximately 2.0. It has been reported that the reaction involving NO as an oxidizer is a termolecular (or trimolecular) reaction (i.e., larger than 2.0). Thus, the reaction in the dark zone is responsible for the NO reduction to produce the final combus-

Table 13. Chemical Compositions of Propellants—A, B, and C.

Propellant	NC	NG	DEP	2NDPA	H_{exp} (MJ/kg)
A	53.0	40.5	4.0	2.5	4.59
B	51.3	39.3	7.0	2.4	4.21
C	48.0	36.7	13.0	2.3	3.47

(a) The percent nitrogen for NC is 12.20%.

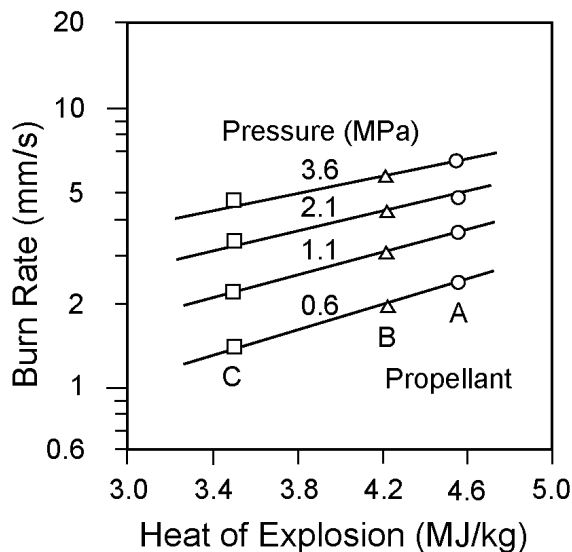


Figure 13. The burn rate of a double-base propellant increases as the heat of explosion increases.

tion product.

The temperature gradient in the fizz zone, $(dT/dx)_{s,f}$, is represented by

$$(dT/dx)_{s,f} = \omega_f Q_f / \rho_p c_p r \quad (34)$$

where Q_f is the heat of reaction in the fizz zone. The reaction rate in the gas phase is given by

$$\omega_f = p^k Z_f \exp(-E_f/RT_f) \quad (35)$$

Substituting equation 35 into equation 34, one obtains the relationship between $(dT/dx)_{s,f}$ and pressure as

$$(dT/dx)_{s,f} = p^{k-n} \quad (36)$$

The results of the measurement of $(dT/dx)_{s,f}$ as a function of pressure show that $k-n$ appears to be constant for double-base propellants and is determined to be $k-n = 0.85$. Thus, the reaction order in the fizz zone is determined to be $k = 1.7$.

As shown in equation 30, the burn rate is dependent on the flame temperature, T_g , at constant pressure. However, the temperature in the dark zone, T_d determines the heat flux feedback from the gas phase to the burning surface of double-base propellants. Since the mixture ratio of NC and NG alters the temperature profile in the gas phase, the heat flux is also altered. Fig-

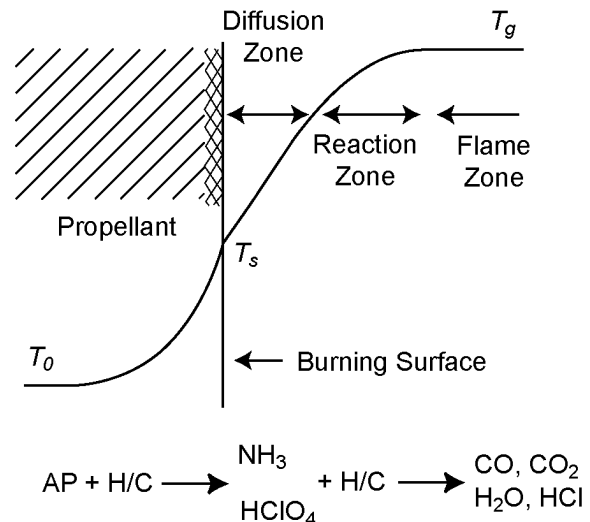


Figure 14. Combustion wave structure of an AP composite propellant.

ure 13 shows the results of the burn rate and pressure relationship as a function of H_{exp} . It is evident that the burn rate of double-base propellants is increased by increases of H_{exp} .

5.5 Combustion of Heterogeneous Propellant

Heterogeneous propellants consist of crystalline oxidizer particles and a polymeric fuel binder. The decomposition process of these materials occurs on and above the burning surface of the propellant. The gaseous oxidizer and the fuel fragments generated at the burning surface diffuse and mix together above the burning surface. This binary diffusion process produces a reactive gaseous fragment that reacts to produce heat and a combustion product.

Figure 14 shows the combustion wave structure of an AP/HTPB composite propellant. Unlike those of a double-base propellant, the surface and gas phase reaction zones are heterogeneous because the AP particles decompose to produce an oxidizer fragment through the reaction process described in Section 3.2, and the HTPB binder decomposes to produce gaseous hydrocarbon fragments at the burning surface. These gaseous fragments diffuse with each other to produce reactive gases that combine to produce its final reaction product. Since the thermochemical properties of AP and HTPB

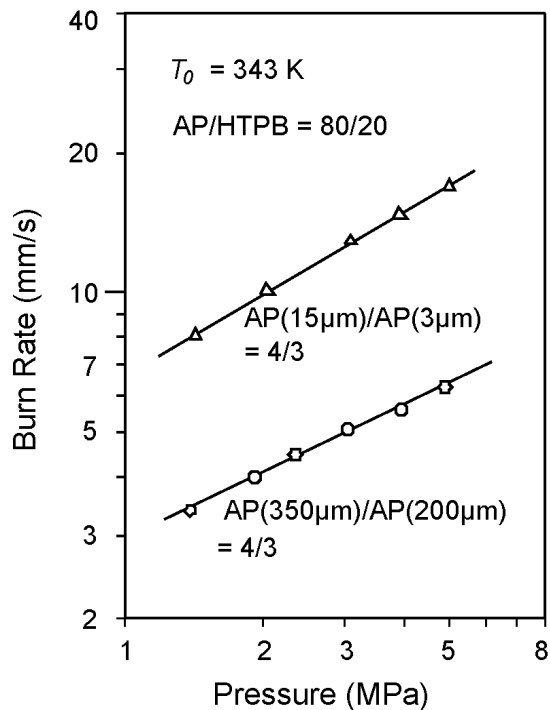


Figure 15. Burn rate of AP composite propellant showing that the burn rate increased with the mixing of fine AP particles.

are different, the temperatures of decomposition are different. In addition, the rates of decomposition of AP and HTPB are also different. Thus, not only the physical structure but also the thermal structure of the burning surface of the propellant becomes heterogeneous. As shown in Figure 14, the time-averaged temperature increases from the initial propellant temperature T_0 to the burning surface temperature T_s , and then to the flame temperature T_g .

The heat feedback from the gas phase to the burning surface is not only dependent on the reaction rate of the reactive gases above the burning surface, but also on the diffusion rate between the oxidizer and fuel fragments. Accordingly, the particle size of the oxidizer plays an important role in the determination of the heat flux feedback from the gas phase to the burning surface. The diffusion rate increases as the AP particle size decreases. As shown in equation 30, the burn rate is dependent on the heat flux feedback to the burning surface. Thus, one can conclude that the burn rate increases as the AP particle size decreases. Figure 15 shows a typical example of burn rate versus pressure

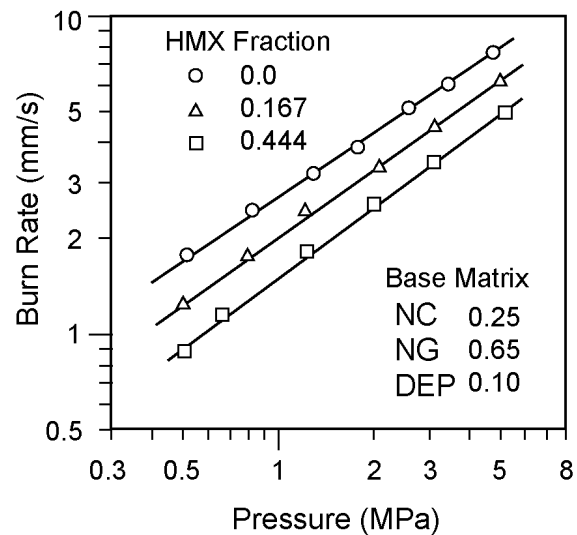


Figure 16. Burn rate of HMX-CMDB propellant as a function of the mass fraction of HMX.

relationship of AP/HTPB composite propellant as a function of AP particle size.

The flame temperature T_f is dependent on the mass fraction of AP, $\xi(\text{AP})$, as shown in Figure 2b. It is shown that T_f increases as $\xi(\text{AP})$ increases at constant AP particle size. However, T_f reaches a maximum at $\xi(0.87)$ and thereafter decreases as $\xi(\text{AP})$ increases. Since the burn rate is dependent on T_f as shown in equation 30, the burn rate becomes a function of $\xi(\text{AP})$. Thus the burn rate increases as $\xi(\text{AP})$ increases in the range of $\xi(\text{AP}) < \xi(0.87)$ at constant AP particle size. Figure 15 shows the results of the effect of AP particle size on the burn rate of AP/HTPB propellants. It is evident that the burn rate increases as the particle size of AP particles decreases at constant $\xi(\text{AP})$. In addition, the burn rate increases as $\xi(\text{AP})$ decreases when the same size of AP particles is used.

As shown in Figure 16, the burn rate of HMX-CMDB propellant increases as pressure increases when $\xi(\text{HMX})$ remains constant. However, the burn rate decreases as $\xi(\text{HMX})$ increases at constant pressure. This indicates that the burn rate decreases as the energy contained within the unit mass of HMX-CMDB propellant increases.

5.6 Combustion of Granulated Propellant

Each grain within a granulated propellant burns independently. When the grains are composed of a double-base propellant used for rockets, the linear burn rate r of each grain appears to be the same as the burn rate of the double-base propellant in a rocket motor. Accordingly, the combustion wave structure of the granulated propellant made of a double-base propellant is the same as that of the double-base propellant. However, the difference between a granulated propellant and a rocket propellant is evident. The mass burn rate m_g of the granulated grains is much faster than that of rocket grains because the burning surface area A_b of the granulated grains is much larger than that of rocket grains as shown in equation 4.

When Black Powder is used as a propellant, the mass burn rate is much greater than granulated single-base and double-base propellants. This is due to the high porosity and small size of each grain of Black Powder. The burn rate is also dependent on the type of charcoal. Various charcoals are made from different types of trees. The porosity of charcoal is dependent on the type of tree used.

In general, granulated propellants are used to eject projectiles from launch tubes such as gun projectiles and to burst fireworks shells because they produce high pressure almost instantaneously. The ejection velocity of a projectile is determined by various parameters: projectile mass, launch tube length, pressure versus time in the launch tube. Detailed examination of the ejection process is accomplished by the analysis of interior ballistics.

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