Burning Rate Characteristics of GAP Propellants

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The burning rate and flame structure of glycidyl azide polymer (GAP)-based composite propellants were examined in order to obtain a wide spectrum of burning rates. Crystalline fine particles of ammonium perchlorate, cyclotetramethylene tetranitramine, or triaminoguanidine nitrate, were mixed within GAP to formulate GAP propellants. Since GAP is an energetic self-sustaining combustible polymer, the burning rate characteristics of GAP propellants appeared to be fundamentally different from those of conventional composite propellants. Measured results indicate that the burning rate, pressure exponent, temperature sensitivity, and flame structure depend largely on the concentration of the crystalline additives. The observed burning rate characteristics were correlated with the concentration of the crystalline particles.

Introduction

GLYCIDYL azide polymer (GAP) is a unique energetic liquid material, which contains $-N_3$ bonds in its chemical structure.[1-4] The terminal OH groups of a GAP are cured with $-NCO$ groups of isocyanates in order to formulate a solidified polymerized material. This energetic polymerized material is termed GAP binder. Since the concentration of oxygen atoms within GAP binder is low, the decomposition and combustion products contain relatively high concentrations of fuel fragments such as C(s), H_2, and CO. Thus, the addition of oxidizers within GAP binder increases the combustion potentials such as the specific impulse of rockets and the impetus of guns. The energetic mixture of GAP binder and crystalline oxidizer particles is the so-called GAP propellant. In this study, the effect of the addition of energetic crystalline oxidizers on the burning rate characteristics of GAP propellant were studied.

Combustion Potential of GAP Propellants

The terminal OH groups of GAP were cured with the NCO groups of hexamethylene diisocyanate (HMDI) and cross-linked with trimethylolpropane (TMP) in order to formulate GAP binder. The GAP binder used as a base matrix of GAP propellants consisted of 84.8% GAP, 12.0% HMDI, and 3.2% TMP. The chemical properties and the theoretical combustion products are shown in Table 1.

The combustion zones of GAP propellants containing crystalline energetic particles are not homogeneous due to the heterogeneous structure of the propellant. During propellant combustion, the crystalline particles interact with the GAP binder which acts as a base matrix surrounding the individual particles. A large number of flamelets are produced on the burning surface of the propellant. Thus, the burning rate behavior is strongly dependent on the physical and chemical mode of the energetic particles and the GAP binder at the burning surface and/or in the gas phase.

The energetic particles studied for GAP propellants were various concentrations of ammoniuim perchlorate (AP), cyclotetramethylene tetranitramine (HMX), and triaminoguanidine nitrate (TAGN). These energetic particles can burn as monopropellants and their products can interact with the products of the GAP binder used. The burning processes of individual energetic particles have been studied previously; however, relatively few studies have been reported on the burning process of the energetic particles within a propellant system.

Since the products of AP are oxidizer rich, they should readily burn with the products of the GAP binder, which are fuel rich. On the other hand, the products of HMX are stoichiometrically balanced, and those of TAGN are fuel rich; therefore, the flame structure of GAP/HMX and GAP/TAGN propellants should be different from the flame structure of GAP/AP propellants. Accordingly, these propellant systems were chosen for study because of the different burning characteristics of each energetic material.

Figure 1 shows the calculated adiabatic flame temperature of GAP propellants as a function of the weight fraction of crystalline energetic materials denoted by ξ. The calculations were based on the JANNAF Thermochemical Tables.[5] It is shown that the flame temperature is the maximum at ξ (AP) = 0.75 for GAP/AP propellant, and the flame temperature of GAP/HMX propellant increases monotonically as ξ (HMX) increases. On the other hand, the flame temperature of GAP/TAGN propellant remains relatively constant when ξ (TAGN) is increased where ξ (TAGN) < 0.65 and the maxium flame temperature is obtained at ξ (TAGN) = 1.0.

Table 1 Chemical properties of GAP binder tested in this study

Chemical formula: $C_{3.3}H_{5.6}O_{1.12}N_{2.63}$
Density (ρ_p) : 1.27×10^3 kg/m^3
Adiabatic flame temperature (T_f) : 1365 K at 5 MPa
Combustion products (mole fractions) at 5 MPa

N_2	C(s)	CO	CO_2	CH_4	H_2	H_2O
19.02	29.83	13.93	0.35	3.68	31.52	1.59

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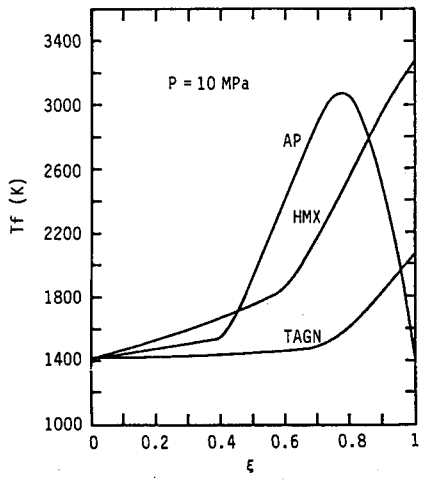

Fig. 1 Adiabatic flame temperature of GAP/AP, GAP/HMX, and GAP/TAGN propellants as a function of ξ.

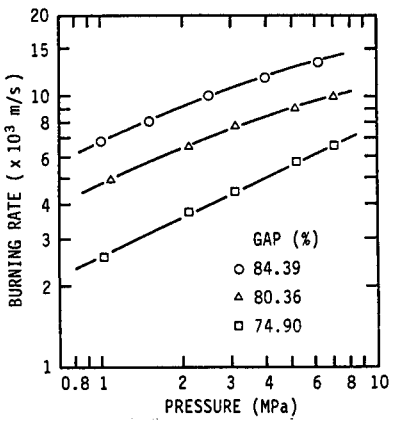

Fig. 2 Burning rate characteristics of GAP binder consisted of GAP, HMDI, and TMP as a function of the concentration of GAP.

Burning Rate and Flame Structure Measurements

The experimental investigations on the burning rate and the combustion wave of GAP propellant were conducted using a chimney-type strand burner that was pressurized with nitrogen. Burning rates were measured at 243, 293, and 343 K, which gave a 100 K temperature difference for the initial propellant temperature.

High-speed microphotographs of the gas phase and burning surface of the propellants were obtained through a transparent window, which was attached on the side of the burner. The methods for the burning rate and flame structure measurements are described in Ref. 6.

Results and Discussion

Burning Rate Characteristics

The burning rates of GAP binder consisting of GAP, HMDI, and TMP without crystalline energetic materials are approximately straight lines on a ℓnp vs ℓnr plot, as shown in Fig. 2, where p is pressure and r is burning rate. The burning rate increases with increasing the concentration of GAP (decreasing the concentrations of HMDI and TMP) mixed within the propellants. The pressure exponent of the burning rate, which is defined by

$$n = (\partial \ell nr / \partial \ell np)_{T_0} \quad (1)$$

at a constant initial propellant temperature T_0, was determined to be 0.35 ~ 0.44. When the initial propellant temperature was increased from 243-343 K, the burning rate increased drastically. The temperature sensitivity of burning rate, which is defined by

$$\sigma_p = (\partial \ell nr / \partial T_0)_p \quad (2)$$

at a constant pressure, was determined to be 0.010/K.

It should be noted that the burning rate of GAP propellant is significantly high compared with conventional composite and double-base propellants, even though the energy contained in the unit mass of GAP propellant is small. Furthermore, the temperature sensitivity of burning rate is also high when compared with other types of energetic solid propellants, such as nitrocellulose (NC)/nitroglycerin (NG) based propellants and ammonium perchlorate based propellants. Table 2 shows a comparison of burning rate, temperature sensitivity, and adiabatic flame temperature T_f of GAP propellant with a conventional NC/NG propellant.[7]

Figure 3 shows the results of burning rate measurements of GAP, GAP/AP, GAP/HMX, and GAP/TAGN propellants as a function of pressure. It is evident that the burning rate of

Table 2 Burning rate characteristics of GAP propellant and a conventional NC/NG propellant (at 5 MPa, T_0 = 293 K)

	GAP	NC/NG
T_f, K	1365	2716
r, × 10^{-3} m/s	10.7	6.9
n	0.44	0.58
σ_p, /K	0.0103	0.0034

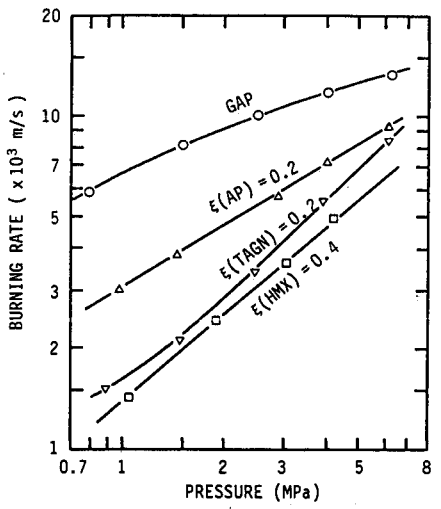

Fig. 3 Burning rate characteristics of GAP/AP, GAP/HMX, and GAP/TAGN propellants.

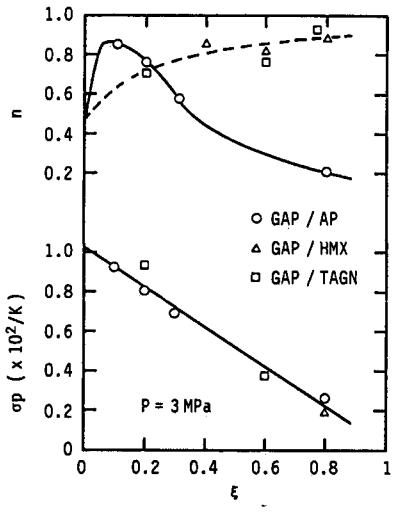

Fig. 4 Pressure exponent and temperature sensitivity of burning rate of GAP/AP, GAP/HMX, and GAP/TAGN propellants.

GAP propellant is decreased by the addition of energetic materials. Similar results of the addition of HMX have been reported by Flanagan et al.[4] The pressure exponent defined in Eq. (1) increases as ξ (HMX) or ξ (TAGN) increases. The pressure exponent of GAP/AP propellant increases with increasing ξ (AP) in the region ξ (AP) $< \sim 0.1$ and decreases with increasing ξ (AP) in the region ξ (AP) $> \sim 0.1$. The temperature sensitivity defined in Eq. (2) decreases monotonically as ξ (AP), ξ (HMX), or ξ (TAGN) increases. The results for n and σ_p are shown in Fig. 4.

It should be noted that σ_p decreases for all the GAP propellants tested in this study. In general, σ_p increases as burning rate increases for NC/NG double-base propellants[7] and for AP-composite propellants.[8]

Figures 5, 6, and 7 show the burning rate characteristics of GAP/AP, GAP/HMX, and GAP/TAGN propellants, respectively, as a function of adiabatic flame temperature. The burning rate decreases rapidly by the addition of AP, HMX, and TAGN particles. Minimum burning rate is observed at ξ (AP) = 0.1 for GAP/AP propellants, at ξ (HMX) = 0.6~0.8 for GAP/HMX propellants, and at ξ (TAGN) = 0.2 for GAP/TAGN propellants. In the region of ξ (AP) > 0.1, ξ (HMX) > 0.8, and ξ (TAGN) > 0.2, the burning rate increases as ξ increases for GAP/AP, GAP/HMX, and GAP/TAGN propellants, respectively. It must be noted that the burning rate of AP without GAP, i.e., ξ (AP) = 1.0, is 7.3×10^{-3} m/s at 3 MPa.

In order to understand the detailed burning rate behavior of GAP/AP propellant, the burning rate is plotted as a function of ξ (AP) at various pressure conditions. As shown in Fig. 8, the burning rate is decreased drastically by the addition of a small amount of AP particles. The burning rate becomes relatively pressure insensitive in regions of low pressure and high AP concentration. The pressure exponent of GAP/AP propellant is shown in Fig. 9 as a function of pressure. The pressure exponent increases with increasing pressure in the region ξ (AP) $< \sim 0.3$. However, the pressure exponent of the propellant containing ξ (AP) = 0.8 remains relatively constant above 2.5 MPa.

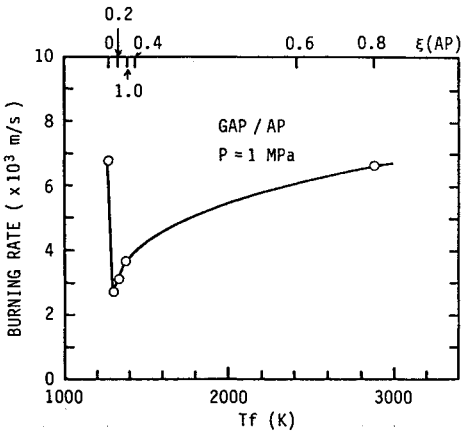

Fig. 5 Burning rate vs adiabatic flame temperature of GAP/AP propellant.

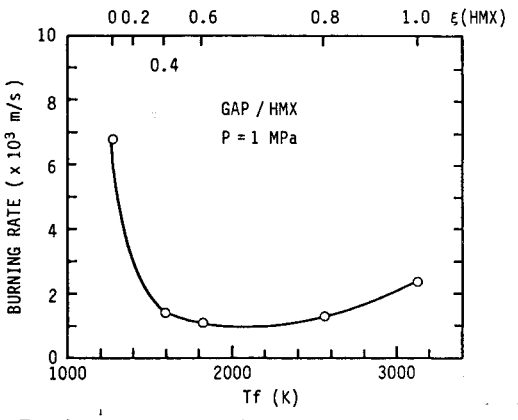

Fig. 6 Burning rate vs adiabatic flame temperature of GAP/HMX propellant.

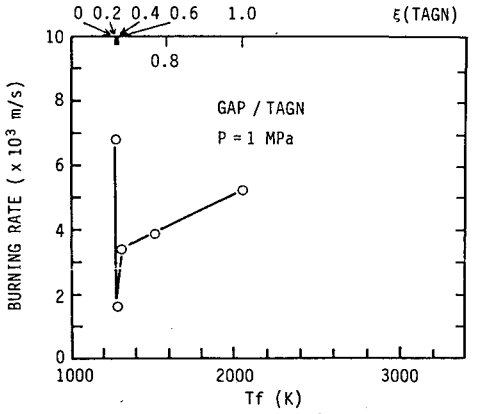

Fig. 7 Burning rate vs adiabatic flame temperature of GAP/TAGN propellant.

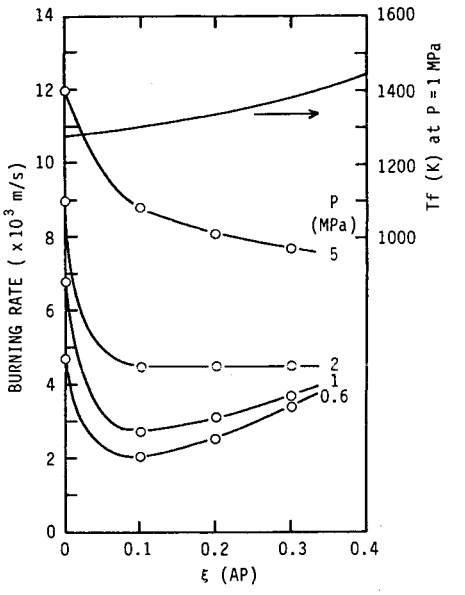

Fig. 8 Burning rate of GAP/AP propellant vs ξ (AP) as a function of pressure.

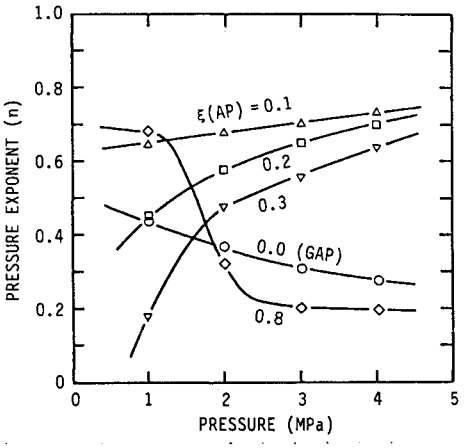

Fig. 9 Pressure exponent of GAP/AP propellant vs pressure as a function of ξ (AP).

Combustion Wave Structures

The combustion processes of GAP propellants were studied using temperature profiles measured in the combustion waves. The temperature profiles give considerable information about the heat transfer mechanism within the combustion zone.

The combustion wave of GAP binder is known to consist of successive thermal zones: nonreactive heat conduction zone, condensed phase reaction zone, and gas phase reaction zone.[3] In the nonreactive heat conduction zone, the temperature increases exponentially from the initial propellant temperature to the decomposition temperature through heat conduction. Decomposition and gasification reaction occurs in the condensed-phase reaction zone just beneath the burning surface. At the burning surface, an exothermic rapid reaction occurs to produce gaseous species. These gaseous species react to raise the temperature in the gas phase reaction zone and to form the final combustion products.

According to the results of the previous studies,[1-4] the exothermic rapid reaction at the burning surface is caused by the decomposition of $C\text{-}N_3$ bonds to form $C \equiv N$ and gaseous N_2. The succeeding reaction process generates C(s), H_2, and remaining gaseous fragments, which act as fuel components above the burning surface of the propellant.

With the addition of AP particles to the GAP matrix, luminous flame streams were produced on and above the burning surface above about 2 MPa. As the concentration of AP was increased, the number of flame streams increased. The flame streams appeared to be produced by the AP particles decomposing at the burning surface. Since the decomposition gas of the GAP binder used as a base matrix is fuel rich and that of AP is oxidizer rich, it is possible that the diffusion between the products of AP and GAP binder shifts in equivalence ratio toward stoichiometric, which results in increased reaction rate and flame temperature.

Significantly different from AP added to the GAP binder, adding HMX to the GAP binder does not alter its flame structure. No diffusion-like luminous streams were seen, unlike the case for AP particles. These results indicate that the fully developed monopropellant flame of HMX or TAGN was not produced on the burning surface. The luminous flame appeared downstream in the gas phase of the GAP/HMX propellant and was caused by the exothermic gas phase reaction of HMX. When the concentration of HMX is low, HMX particles probably sublimate endothermically at the burning surface and reduce the overall heat of reaction generated at the burning surface. This reaction is responsible for the reduced burning rate of GAP/HMX propellants when ξ (HMX) is small.

As the concentration of HMX increases, the luminous flame produced above the burning surface approaches the burning surface. The heat flux transferred back from the gas phase to the burning surface increases, and the burning rate increases as ξ (HMX) increases. Since the decomposition and combustion process of TAGN is similar to that of HMX, the burning rate behavior of GAP/TAGN propellants appears to be similar to that of GAP/HMX propellants.

Conclusions

The burning rate of GAP propellant decreases drastically by the addition of AP, HMX, or TAGN in the range of $\xi < \sim 0.3$. Minimum burning rate is observed at ξ (AP) = 0.1 for GAP/AP propellants, at ξ (HMX) = $0.6 \sim 0.8$ for GAP/HMX propellants, and at ξ (TAGN) = 0.2 for GAP/TAGN propellants. The burning rate increases gradually with increasing ξ in the regions of ξ (AP) > 0.1, ξ (HMX) > 0.8, and ξ (TAGN) > 0.2.

The flame structure of GAP propellants is altered by the addition of AP. A large number of flame streams are produced by the diffusional mixing of the decomposed gases of the AP particles and the GAP binder used as a base matrix. Thus, the gas phase structure of GAP/AP propellants appear to be highly heterogeneous. On the other hand, the HMX and TAGN particles melt and gasify to form homogeneously mixed reactive gases on and above the burning surface of GAP/HMX and GAP/TAGN propellants. Accordingly, the gas phase structures of GAP/HMX and GAP/TAGN propellants appear to be homogeneous.

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