Engineering Notes

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Ignition Delay Studies on Hybrid Propellants

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Introduction

In a recent publication,[1] a brief study of the thermal and ignition behavior of solid hydrazones and azines was reported. Some of the phenylhydrazones were found to be igniting spontaneously on coming into contact with red fuming nitric acid (RFNA). Besides having small ignition delays, these compounds generally are more energetic than the usual solid amine-based fuels[2-4] and therefore should serve as attractive solid fuels for hybrid rocket systems. Because the ignition delay (ID) of a hybrid propellant system is dependent upon several factors such as oxidizer-to-fuel ratio, concentration of nitrogen dioxide in RFNA, particle size of the fuel, etc., the present study was undertaken to evaluate the effect of these parameters. The results have been compared with those of solid amines/RFNA systems.

Experimental

Ignition Delays

All ignition delays were measured at room temperature (25° ±2°C), using a simple device set up in the laboratory. The liquid oxidizer taken in a graduated tube was dropped, virtually as a single drop, onto the fuel kept in a crucible. The appearance of the flame was detected using a phototransister circuit. The time lapsed between the release of the oxidizer and the appearance of the flame was recorded using an electronic counter. The oxidizer drop time, obtained by a separate experiment, was found to be 101 ±0.5 msec, which was subtracted from the total to get the actual ignition delays.

Materials

RFNA having a 25.2% NO_2 and anhydrous nitric acid were supplied by M/s Purex Laboratories. RFNA having lower concentrations of NO_2 was prepared by removing NO_2 by bubbling dry air through the acid. The phenylhydrazones were prepared by reacting phenylhydrazine with the appropriate aldehyde in 1:1 mole ratio. The compounds were recrystallized from alcohol, and their purity was ascertained by comparing their melting points with those reported in the literature. The fuel powders were seived through stainless steel seives to get the required particle sizes.

Results and Discussion

Of the various aldehyde-phenylhydrazones tried, furfuraldehyde-phenylhydrazone (FPH) and 4-dimethylaminobenzaldehyde phenylhydrazone (DBPH) were found to be quite promising as far as their ignition delays are concerned. Experiments to determine the critical relative amounts of fuel and oxidizer for minimum ignition delays are presented in Table 1. It is seen that each fuel has a minimum ID at a particular oxidizer-to-fuel ratio. The hydrazones have smaller ignition delays than benzidine.

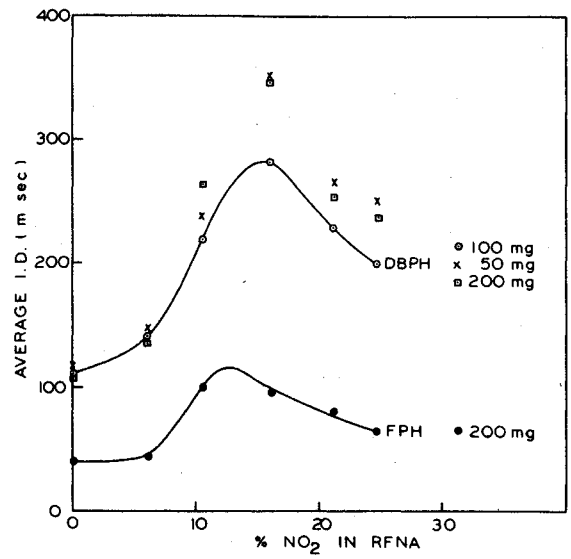

Fig. 1 Effect of NO_2 concentration in RFNA on the ignition delays of phenylhydrazones (RFNA, 0.55 ml).

Table 1 Effect of relative amounts of fuel and oxidizer on ID

Weight of fuel, mg	Average ID, msec		
	FPH[a]	DBPH[a]	Benzidine[b]
50	38.3	234	...
100	28.5	181	1102
150	...	...	634
200	21.8	231	488
250	...	...	563
300	27.1	266	591
400	42.9	...	...

[a] Quantity of RFNA, 0.55 ml (21.50% NO_2); particle size, 250-106 μ.
[b] Quantity of RFNA, 0.50 ml (21.6% NO_2); particle size, 226-180 μ.

Table 2 Effect of particle size on the ID of phenylhydrazones

Particle size, μ	Average ID, msec	
	FPH, 200 mg; RFNA, 0.55 ml (21% NO_2)	DBPH, 100 mg RFNA, 0.55 ml (24% NO_2)
420-300	126	231
300-252	121	212
252-212	115	201
212-152	...	192
152-125	122,225[a]	191
125-106	236,435[a]	184
106-74	256,705[a]	195,236[a]
74-53	277,740[a]	206,262[a]

[a] Value corresponding to second flame.

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Table 3 Effect of particle size on the ID of amines

Particle size, μ	Average ID, msec: Benzidine, 350 mg; RFNA, 0.5 ml (21.6% NO_2)	Average ID, msec: *p*-phenylenediamine, 300 mg; RFNA, 1 ml (8% NO_2)
453-377	767	205
377-226	580	165
226-180	490	97
180-120	477	...
120-85	640,3227[a]	219, 531[a]

[a] Value corresponding to second flame.

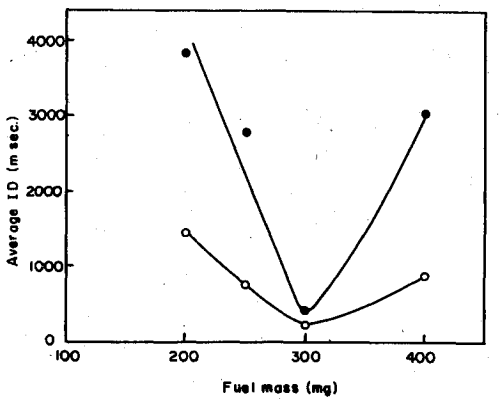

Fig. 2 Effect of relative amounts of fuel and oxidizer on the ignition delays of *p*-phenylenediamine [particle size, 120-80 μ; RFNA, 1 ml (8% NO_2); ○, first flame; ●, second flame].

The variation in ignition delays with the concentration of NO_2 in nitric acid is plotted in Fig. 1. It is seen that FPH and DBPH both give least ignition delays with the pure anhydrous acid, rather than RFNA. The ignition delays are maximum around 12-16% NO_2 concentration in the acid. Figure 1 also shows that the oxidizer/fuel ratio for minimum ignition delays does not change significantly with the NO_2 concentration. The effect of particle size of the fuel on the ID of FPH and DBPH is presented in Table 2. It appears that the ignition delays decrease only marginally up to a certain particle size when one goes from coarse to fine particles. The fuel burns readily in this region, giving highly reproducible ignition delays. The minimum delays are observed at particle sizes of 252-212 and 125-105 μ in the cases of FPH and DBPH, respectively. Below these particle sizes again, longer ignition delays are observed, and the ignition of the fuel becomes erratic. The ID values observed in this fine-particle-size region may be divided into two distinct sets, probably corresponding to two flames. The first flame appears but is not permanent and extinguishes soon. The second flame, which appears later, is steady and lasts until the fuel and/or oxidizer is consumed. The phototransister circuit senses sometimes the first flame and sometimes the second, and therefore two sets of values of the ignition delays are obtained.

A similar effect was observed in the case of amine fuels, benzidine, and *p*-phenylenediamine. As shown in Table 3, the ignition delays of these systems decrease up to a certain particle size, v.z. 150 μ, below which the ignition becomes erratic, resulting in two flames. In the case of benzidine, because of considerable time lag, the two flames could be distinguished visibly by the naked eye and could be photographed using a storage oscilloscope. In order to observe this phenomenon more carefully, we studied the ignition behavior of finely powdered (particle size, 120-85 μ) *p*-phenylenediamine/RFNA system as a function of oxidizer-to-fuel ratio. As expected, two ID values corresponding to two flames are obtained at each oxidizer-to-fuel ratio, as shown in Fig. 2. It therefore appears to be a general phenomenon for fine powders.

References

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Estimate of Pressure Distribution on Launch Vehicles at Small Angles of Attack

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Nomenclature

C_p = coefficient of pressure
C_{p0} = leeward side coefficient of pressure
$C_{p\pi}$ = windward side coefficient of pressure
M = Mach number
X/L = nondimensional axial coordinate
α = angle of attack
γ = specific heat ratio
θ_b = body parameter
θ_v = turning angle
ϕ = circumferential angle

Subscripts

A = location on the body (or afterbody) after acceleration (or expansion) starting point
F = location on the body (or afterbody) before acceleration (or expansion) starting point
∞ = freestream

FRIBERG and Walchner[1] predicted the hypersonic pressure distribution on axisymmetric blunt slender cones for any circumferential angle, using the formula

$$C_p(\phi) = \tfrac{1}{2}\left[(C_{p0}/2)^{1/2}(1+\cos\phi) + (C_{p\pi}/2)^{1/2}(1-\cos\phi)\right]^2 \quad (1)$$

where, for small values of $(\theta_b \pm \alpha)$,

$$C_{p0,\pi} = 2(\theta_b \pm \alpha)^2 \quad (2)$$

The Newtonian impact values of Eq. (2) for the leeward and windward sides were replaced by measured values in their analysis. McBrayer[2] utilized empirical correlation plots and improved the accuracy of the tangent cone method.

In applying these formulas to the blunt nose cose and flare of a launch vehicle, it is assumed that C_p at zero angle of

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