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Technical Notes

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Combustion Effects of C_{60} Soot in Ammonium Nitrate Propellants

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Introduction

COMPARED to perchlorates, inorganic nitrates such as ammonium nitrate (AN) perform relatively poorly as oxidizers. For AN, an important reason for this poor performance is that the molecule can exist in five crystalline states. Differential Thermal Analysis (DTA) results have shown that polymorphic phase transitions occur at temperatures of −18, 32.1, 84.2, and 125.2°C, defining the five states. The transition at 32.1°C is accompanied by a large decrease in density, which during repeated thermal cycling at ranges close to room temperature can lead to irreversible growth and cracking in solid grains containing AN, causing improper burning. Adding phase stabilizers such as nickel oxide and maintaining dry conditions during processing and storage can alleviate this problem somewhat. However, this is somewhat challenging due to the extremely hygroscopic nature of AN. AN also undergoes a melt transition at 169.6°C. This liquid phase exists until vaporization at 210°C. The presence of this liquid phase is also a contributor to the list of burning rate limiting factors that are inherent with AN. Note that all of these transitions are endothermic.

Several investigators[1–5] have shown that the combustion and pyrolysis behavior of AN can be altered in the presence of various forms of carbon combined with other additives. Because carbon is a rather benign additive in terms of hazardous byproducts (or lack thereof) these results provide a possible method of modifying the performance of AN-based propellants. Carbon fullerene (C_{60}) is a form of carbon that has been shown to have reactivity greater than regular carbon black. This is due to the large amount of energy tied up in the complex crystalline bond structure. A comparison of DTA–thermogravimetric analysis (TGA) plots[6] is an indication of this through 1) the lower initiation temperature for onset of weight loss for fullerene (650°C for carbon and 425°C for fullerene) and 2) the higher heat release indicated by an increase in differential temperature. Unfortunately, carbon fullerene is an expensive commodity. However, DTA–TGA[6] tests of fullerene soot, a by-product of the carbon fullerene manufacturing process, show a potentially higher reactivity than both carbon black and pure fullerene. TGA results show that the fullerene soot has an initiation temperature of 390°C, which is lower than both carbon black and pure fullerene. Thus, we propose that the use of fullerene in an AN-based propellant may provide an increase in burning rate in the same manner as carbon addition. Furthermore, if the initial carbon reaction pathway leading to the noted burning rate increase is the rate limiting step, then the use of the more reactive form of carbon should provide an increase beyond that of regular carbon.

Approach

Two quantitative techniques were used in this experimental study to learn about the impact of fullerene soot on AN combustion. The first was the measurement of propellant decomposition behavior through the use of a differential scanning calorimeter (DSC). The second was the determination of the propellant ballistic properties (burning rate, pressure exponent) over a range of chamber pressures (nominally from 5 to 30 MPa) through the use of an ultrasonic propellant burner.[7,8] Additionally, the extinguished surfaces of the propellants were examined in an attempt to gain insight into changes in the surface morphology during combustion due to the variation of the propellant chemistry.

Table 1 shows the formulation matrix that was used in the study related to the changes to a baseline formulation. The baseline formulation for this study was propellant 1 (PM-97-025), which consisted of 65% 54-μm Permaline AN in an 8% polyglycol adipate analog binder with 7.3% BTTN and 17.1% TMETN energetic plasticizers using 1.6% hexamethyl diisocyanate as a curative. Propellants A and B substitute carbon black or C_{60} for the binder. Propellant A and B then give a direct comparison between either carbon black and C_{60} at 65% AN level.

The DSC system used in this study is capable of measuring the heat flow over a range of temperatures from −20 to 400°C with a temperature accuracy of better than ±1.5°C and an enthalpy reproducibility of ±1%. The 2–8 mg samples were sealed in small, vented aluminum crucibles. The temperature range was 30–375°C at a heating rate of 15°C/min. The entire cell was placed inside a nitrogen-purged, insulated vessel.

An ultrasonic pulse–echo technique measured the thickness of a burning propellant sample as a function of time and pressure in a closed bomb. The propellant samples used for the burning rate measurements were nominally 2.5-cm cubes or 2.5-cm cylinders weighing approximately 100 gm. The sides were inhibited with a thick layer of epoxy. The thickness of the propellant is determined by measuring the time lapse between the emitted pulse and the received wave via an ultrasonic emitting/receiving transducer. When the time derivative of the thickness measurements is taken, the burning rate

Table 1 Propellant formulations

Propellant	Propellant designation	% AN	% C	% C_{60} soot	% BTTN/ TMETN
PM-97-025	1	65	0	0	25
PM-97-028	A	65	5	0	20
PM-97-071	B	65	0	5	20

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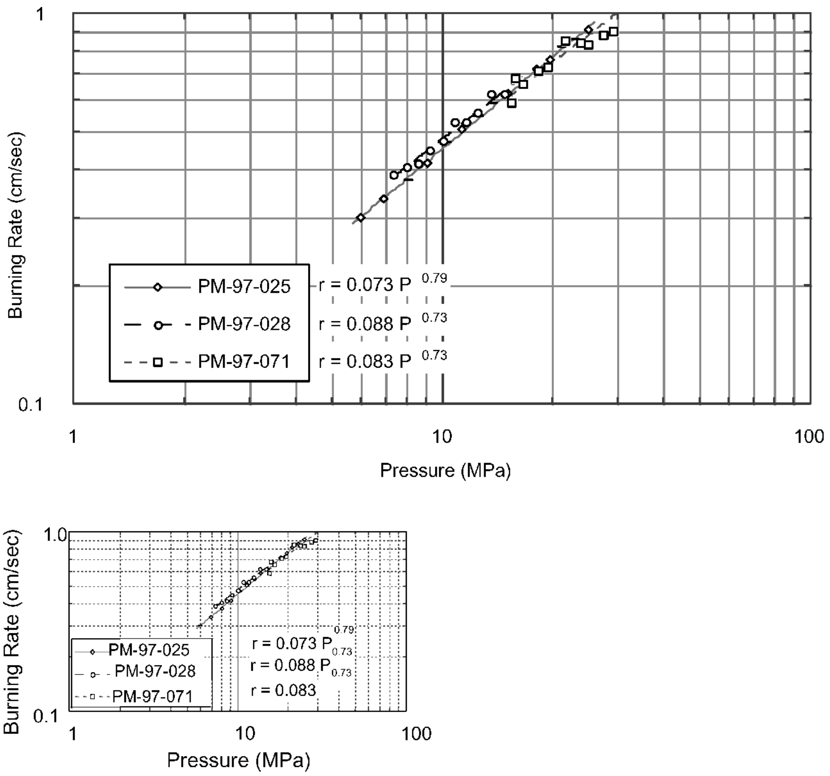

Fig. 1 Comparison of burning rates for propellants 1, A, and B.

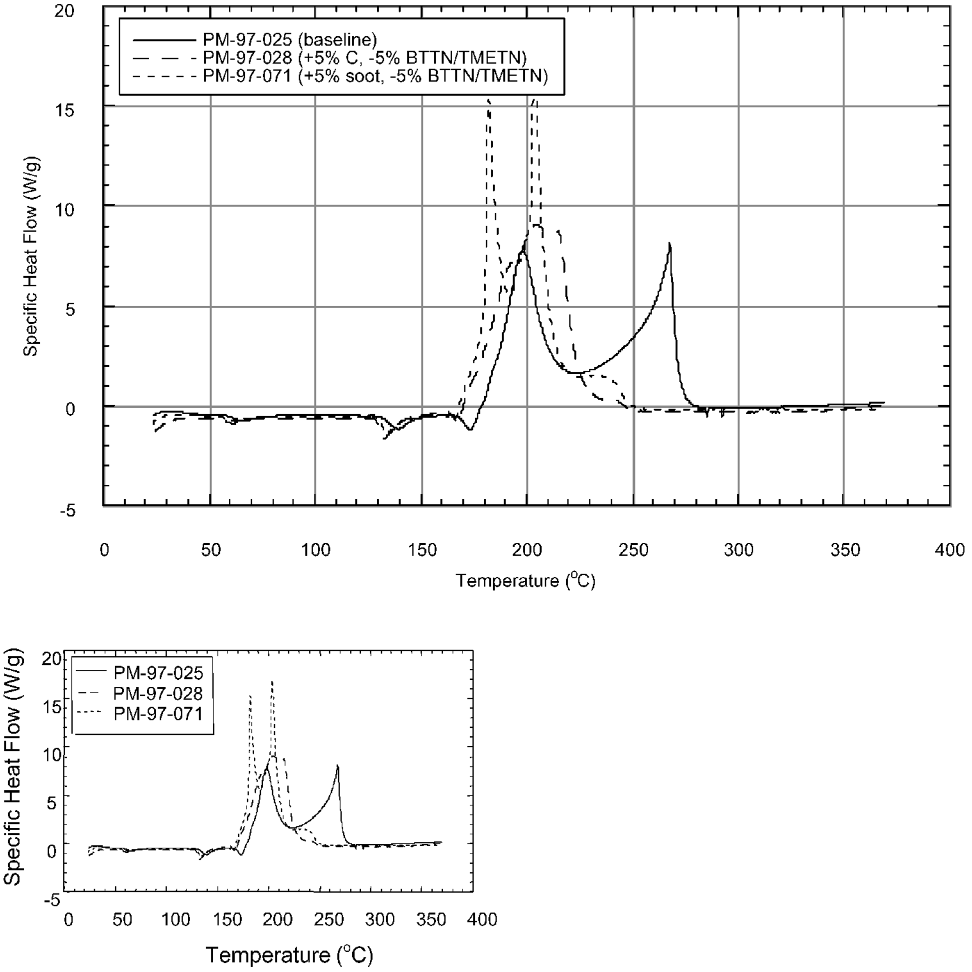

Fig. 2 DSC plots for propellants 1, A, and B.

is determined. Because the ultrasonic propellant burner is a closed vessel, the burning rates can be correlated with the increasing burner pressure.

Results and Discussion

Figure 1 shows the ballistic results for propellants 1, A, and B. The burning rates show no significant alteration among the three propellants. The differential scanning calorimetry plots for these three propellants shown in Fig. 2 tell a different story, however. Compared with the baseline, both the carbon and the fullerene soot appear to eliminate the secondary exothermic peak at approximately 275°C. Both also seem to have exothermic activity centered around the BTTN/TMETN exotherm at 200°C. The existence of the double exotherms for the soot propellant B (-071) as opposed to the single exotherm for the carbon black propellant A (-028) can be accounted for by recalling that the fullerene soot contains a variety of carbon molecular forms, with different structures and volatilities.

Examination of the optical microscope photographs of the extinguished surfaces of the two modified propellants also revealed a substantial change from the baseline. The surfaces for propellants A (-028) and B (-071) were dry, with no evidence of the AN melt layer noted in propellant 1 (baseline). Based on the absence of the second exotherm for propellants A and B, it is evident that the exotherm is due to a reaction between BTTN/TMETN decomposition products and the AN melt layer. This is supported by the fact that, in the baseline propellant, which has a thick melt layer, the second exotherm shows a sharp drop at ~270°C, corresponding to the rapid drop of the vaporization endotherm for the AN melt. If the melt layer is eliminated, then so is the exotherm.

From a purely qualitative standpoint, the trade of carbon and fullerene soot for the nitrate esters has a substantial effect on the condensed-phase behavior and surface morphology of the AN propellant compared to the baseline. However, no measurable effect is evident in terms of burning rate behavior, or dominance of the flame kinetics over diffusion mechanisms. There are two possible reasons for this behavior: 1) The gas-phase energy release dominates any condensed-phase contribution to the overall chemical energy release or 2) any benefit gained from carbon or fullerene enhancement of AN combustion is masked by elimination of the second exotherm when the BTTN/TMETN is reduced. What is clear is that for this propellant/binder system, elimination of the melt layer or changes in the condensed phase reactions do not significantly alter the ballistics. Additionally, although the fullerene soot has a different effect than carbon on the condensed-phase behavior of the AN/BTTN/TMETN propellant when exchanged for the plasticizer, its effect is not substantially different from carbon on the propellant ballistics.

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Performance Analysis of Short Takeoff and Vertical Landing Aircraft Nozzle in Hover

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Nomenclature

A = cross-sectional area
k = specific heat ratio
M = Mach number
$\dot{m}$ = mass flux
P = pressure
q = dynamic pressure
R = gas constant
T = temperature
V = velocity

Subscripts

t = total
0 = far upstream
8 = nozzle throat
9 = nozzle exit

Introduction

FOR the propulsion system of a short takeoff and vertical landing (STOVL) vehicle such as the F-35 joint strike fighter (JSF), good propulsive efficiency[1] at high speeds dictates a high-velocity thrust stream, whereas efficient hover operation is achieved by propelling a large mass of low-speed air. The exhaust flow conditions in hover are radically different from those in transonic acceleration; however, the nozzle provides the same flowpath for both (Fig. 1). The F-35 nozzle is scheduled to provide an internal expansion ratio of 1.3 to give good performance for transonic acceleration. This nozzle expansion ratio is also presented in hover that produces over-expansion, resulting in significant thrust loss. For the three important mission points of transonic cruise, acceleration, and hover, the nozzle pressure ratio (NPR) are 3–4, 6–8, and 2, whereas the respective exhaust temperatures are 780, 2000, and 780 K.

Nozzle Performance Analysis

The nozzle gross thrust

$$F_g = \dot{m}V_9 + (P_9 - P_0)A_9 \tag{1}$$

is maximized when the flow is expanded to ambient pressure, this being governed by the nozzle geometry. Cruise produces a cool,

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