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Mechanism of Modifying Ballistic Properties of Propellant Formulations by Fast-Burning Inclusions

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ABSTRACT

The combustion characteristics of binary compositions of fast-burning energetic materials (FBEM) with main composite propellant components like ammonium perchlorate (AP) and polymeric binders have been studied in a constant pressure bomb, and combustion mechanism has been proposed. Combustion behaviour of composite propellants containing granulated FBEM of different particle sizes has been investigated. FBEM additives as high as 40 per cent of fine particle size to a composite propellant have not been shown to influence markedly the burning rate, whereas incorporation of FBEM grains of 500 μm particle size allows not only a considerable increase in the burning rate but also modifies the burning rate-pressure dependence. A mechanism of combustion of propellant compositions containing FBEM grains has been evolved that allows criteria for FBEM performance and combustion stability.

NOMENCLATURE

AP	Ammonium perchlorate
a_o	Mass fraction of crystalline component
d	Fast-burning additive grain size
d_o	Particle size of crystalline component
d_c	Critical diameter of combustion
d_p	Pore size
E	Activation energy
FBEM	Fast-burning energetic material
GP	Guanidine periodate
K_p	Criterion for performance
K_s	Criterion for combustion stability
LDNP	Lead 2,4-dinitrophenol
LTNC	Lead 2,4,6-trinitro-meta-cresole
l	Unit volume size
n	Proportionality constant
P	Pressure
R	Universal gas constant
T_f	Flame temperature
U	Burning rate of propellant
U_{FBEM}	Burning rate of fast-burning energetic material

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U_p	Burning rate of base-line propellant
W	Burning rate of propellant composition containing fast-burning inclusions
z	Ratio of propellant burning rate to FBEM burning rate
α	Volume fraction of fast-burning additive
γ_o	Crystalline component density
δ	Apparent density of crystalline component in mixture
X	Thermal diffusivity
ρ	Charge density
	Combustion time of unit volume
τ_d	Ignition delay time

1. INTRODUCTION

The problem of increasing the burning rate (U) of rocket propellants and controlling the burning rate-pressure $U(P)$ dependence has emerged coincidentally with their advent and evolution. For the most part, this problem can be solved by the use of various combustion catalysts[1,2]. However, there comes a point where all burn rate catalyst possibilities have been exhausted, but the wanted burning rate level has yet to be reached. In such cases, one can employ various additives[3,5] which possess the burning rate of their own several times superior to that of the starting propellant composition. It is not clear how the particle size, burning rate, and content of additive entered into a propellant composition can influence the burning rate level and a character of burning rate-pressure dependence. However, the effect on the burning rate of entering various fast-burning energetic materials (FBEM) into ammonium perchlorate (AP)-polymeric binder propellant formulations has been studied.

2. EXPERIMENTAL DETAILS

A window constant pressure bomb (2.5 l) has been used to measure the burning rate of compositions in the pressure range 0.1-40 MPa. The bomb was pressurised with nitrogen. The burning rate behaviour were registered using a slit-camera. As a rule, uncured propellant specimens were used for testing, since the difference in the burning rate between cured and uncured specimens had been shown to lie within the limits of experimental error (± 2.5 per cent). In preparing the strands, a propellant composition was put into transparent acrylic tubes 7 mm (i.d.), 30-50 mm (height). Fast-burning components were added to a propellant composition preheated to 80 °C.

The delay time of ignition (τ_d) of the propellant layer immediately under a FBEM grain was determined using strands separated into two parts with a pressed FBEM tablet ≈1 mm thick and 7 mm diameter. The slit-camera recorded the front-of-flame propagation through the propellant-FBEM tablet-propellant strand section.

Powdered binary mixtures of FBEM with crystalline propellant ingredients and solid substances were compacted into acrylic tubes 7 mm (i.d.) at 100-200 MPa to give pressed strands with relative density of 0.95-0.98. Grains of FBEM were prepared by granulating tablets pressed at 200-500 MPa followed by sieving. The thick of the tablets normally determined the desired FBEM grain size. The following energetic materials were used as the fast-burning additives for which combustion had been studied[6]: Lead salts of 2,4-dinitrophenol (LDNP) and 2,4,6-trinitro-meta-cresol (LTNC), and guanidine periodate (GP).

3. RESULTS & DISCUSSION

Firstly, consider the effect of LDNP and LTNC contents on the propellant burning rate The lead salts are of fine particle size (< 10 µm) and burn at 16 and 22 cm/s at 10 MPa, respectively. Incorporation of 20 per cent LTNC into a propellant, which burned at 1.8 cm/s at 10 MPa, resulted in only 18 per cent increase in the burning rate, whereas addition of the same amount of LDNP even lowers it (Fig.1). If one uses a propellant composition burning at 6.6 cm/s at 10 MPa, both LDNP and LTNC entered reduces the burning rate. The higher the burning rate of base-line propellant, the more is the decrease in the burning rate of the

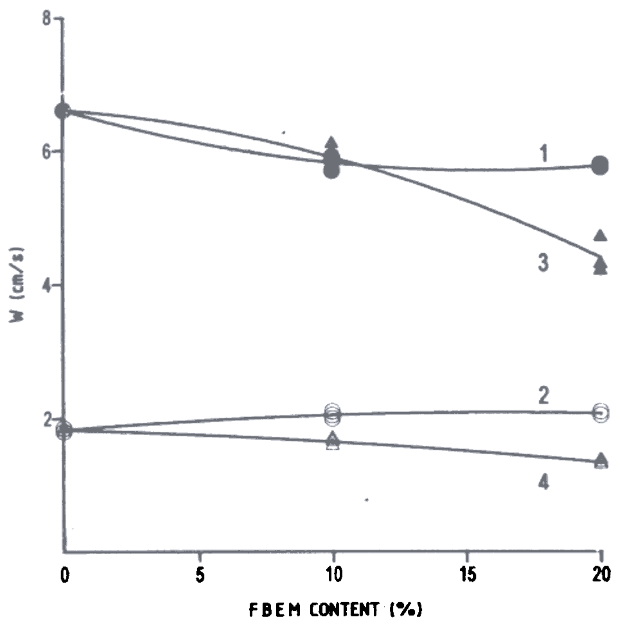

Figure 1. Effect of FBEM content on the burning rate of AP-based composite propellants at 10 MPa. Fast-burning additives: LTNC (1, 2) and LDNP (3, 4). FBEM particle size (< 10 μm).

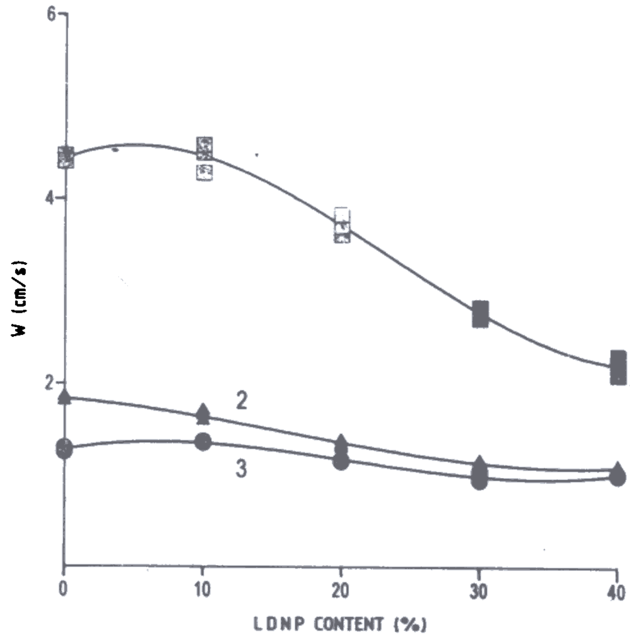

Figure 2. Effect of LDNP content on the burning rate of AP-based composite propellants at 10 MPa. LDNP particle size (< 10 μm).

resulting composition (Fig. 2). Even 40 per cent LDNP added fails to enhance the burning rate. For such observations, binary mixtures of FBEM with main propellant ingredients, AP and polymeric binder have been examined wrt effecting the burning rate.

Mixtures of LDNP and LTNC with 60 per cent AP (160 - 250 μm) particle size exhibit practically the same burning rate as pure lead salts (Fig.3). The presence of AP significantly alters the flame luminosity, keeping the burning rate level essentially unchanged. While LDNP combustion produces deep-red flame and copious soot formation, its mixtures with AP demonstrate a dazzling flame and no soot in the combustion products. This means a profound effect of AP on gas-phase reactions with a little or no effect on the burning rate-limiting zone. If this is the case then changing the AP to an oxygen-free solid should exert no effect on the burning rate too. Experiments with mixtures containing 50 per cent *KCl* (160-250 μm) particle size really show the same burning rates as for pure LDNP, LTNC and mixtures thereof with AP at all pressures tested. The luminosity during combustion of *KCl*-based mixtures is faint. By this means neither the chemical nature of a crystalline component nor its content in the mixture (within the range 0-80 per cent) has been shown to affect the burning rate of binary compositions of FBEM.

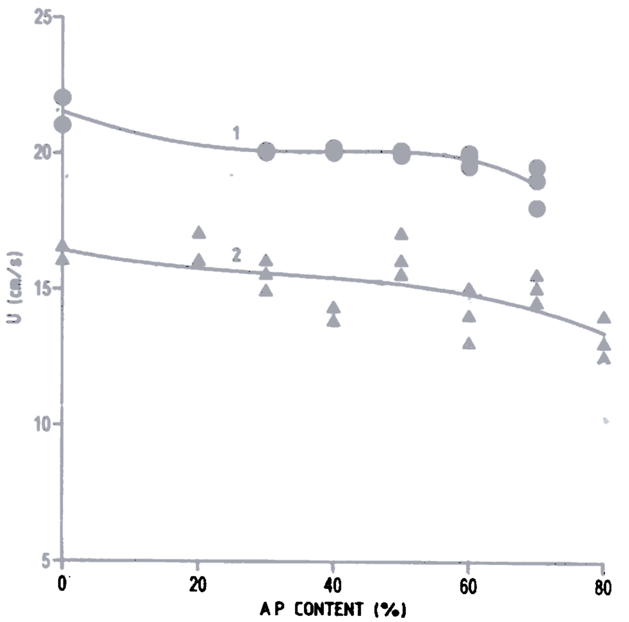

Figure 3. Effect of AP content on the burning rate of binary mixtures with LTNC (I) and LDNP (2) at 10 MPa. AP particle size (160-250 μm).

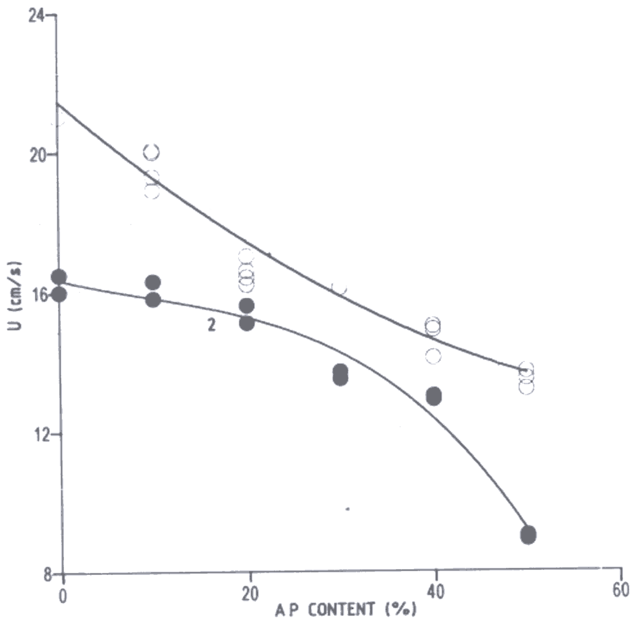

Figure 4. Effect of AP content on the burning rate of binary mixtures with LTNC (1) and LDNP (2) at 10 MPa. AP particle size (approx 1 μm).

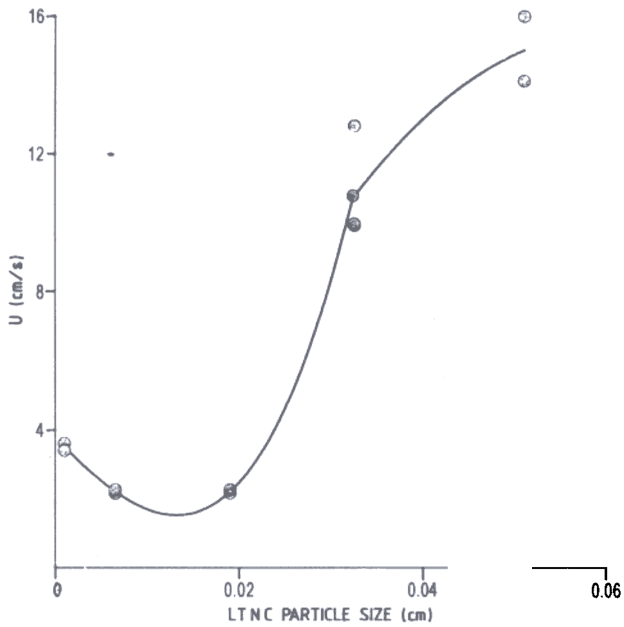

Figure 5. Effect of LTNC particle size on the burning rate of binary mixture with polyester at 10 MPa. Polyester content 20%.

To gain insight into why the addition of an inert solid as high as 50-80 per cent to the FBEM keeps the burning rate practically unchanged, one may assume that the combustion process propagates only over FBEM particles confined between larger particles of the crystalline component, serving as if they were capillary tubes. In this case, a crystalline component will influence the burning rate of FBEM, provided that the pore size between its particles (d_p) is close to the critical combustion diameter (d_c) of FBEM combustion.

In order to estimate the d_p, the following equation[7] may be used:

$$d_p = \frac{2\,(1-\delta)\,d_o}{3\delta} \tag{1}$$

where d_o is the particle size of crystalline component, δ is the apparent density of crystalline component in the pressed charge (as if the pores between particles were unfilled with FBEM). The latter is defined by

$$\delta = \frac{\rho . a_o}{\gamma_o} \tag{2}$$

where ρ is the charge density, γ_o is the crystalline component density, and a_o is the mass fraction of the crystalline component in the mixture. To make a rough estimate of the critical combustion diameter (d_c) , the following equatlon[8] can be employed:

$$d_c = \frac{2X}{U_{FBEM}} \sqrt{\frac{8eE}{RT_f}} \tag{3}$$

where X is the thermal diffusivity, E is the activation energy, T_f is the flame temperature, and R is the universal gas constant. Assuming that $x = 1.10^{-3}$ cm^2/s, E=3 5 kcal/mole, and T_f=2500 K, we obtain d_c =2 5.10^{-3} /U_{FBEM}.

From the above discussion, it follows that the crystalline component will not influence the burning rate of FBEM, if the ratio $A = d_P/d_c$ is more than unity, that is

$$A = \frac{27(\gamma_o - \rho a_o) d_o U_{FBEM}}{\rho a_o} > \tag{4}$$

Calculations for mixtures of LDNP and LTNC with AP, KCl, $KClO_4$ indicates A>1 for all cases when the burning rate of the mixtures is close to that

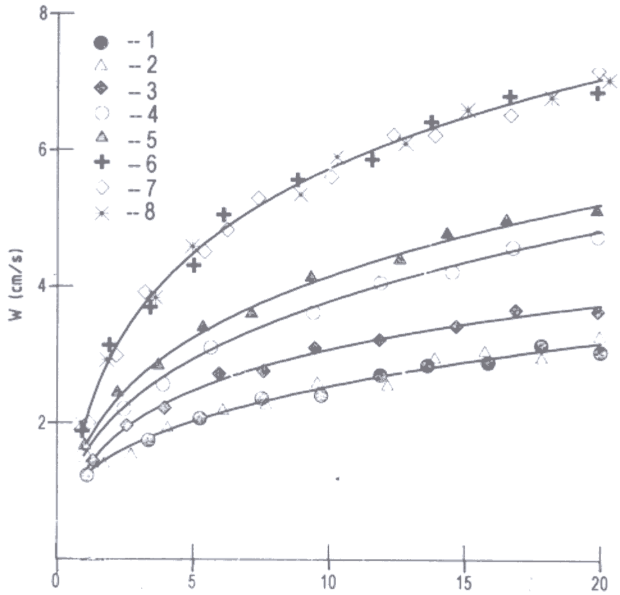

Figure 6. Burning rate *vs* pressure for a composite propellant containing 15 per cent LTNC grains at different LTNC particle sizes: < 10 μm (2), < 100 μm (3), 200-315 μm (4), 315-400 μm (5), 400-630 μm (6), 630-800 μm (7), 800-1000 μm (8). Base-line propellant (1).

of the pure lead salts. It follows from Eqn (4) that smaller the particle size of the crystalline component, the lesser is its content in the mixture at which it can influence the burning rate. Figure 4 shows that even minor contents of AP with ≈μm particle size lower the burning rate of both LDNP and LTNC.

On addition of such binders as thiokol, polyesters, divinyl rubber, and epoxy resin to LDNP and LTNC, the burning rate appears to drop abruptly. A mixture of LDNP with 20 per cent polyester burns slower than pure LDNP by a factor of 20. Addition of 5 per cent polyester decreases the burning rate by a factor of 2-3. Other polymeric binders considered showed a similar behaviour. This is due to the fact that a binder separates and covers small (<10 μm) FBEM particles. In doing so, each isolated FBEM particle is incapable of sustained burning as its size is smaller than the d_c. This can explain why an addition of even 40 per cent fine crystalline FBEM to a propellant composition did not increase the burning rate. Increasing the particle size of FBEM, by the use of granulated pellets, causes the burning rate to increase. The burning rate of a mixture composed of LTNC grains and 20 per cent polymeric binder approaches that of pure LTNC (Fig 5).

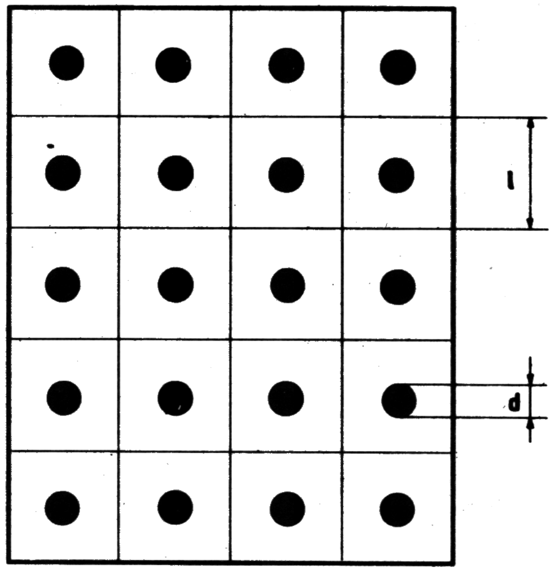

Figure 7. Schematic of distribution of FBEM grains in a propellant composition. (*l*) Size of unit volume, (d) - FBEM grain size.

It follows from these results that the FBEM particle size should exceed some critical dimension for the burning rate of the composition to be enhanced. Figure 6 shows that an increase in the LTNC particle size to 500 μm leads to a progressive enhancement of the burning rate of the propellant composition containing 15 per cent LTNC grains. On further increasing the particle size, the burning rate of the composition remains practically unchanged.

In order to explain the results observed, consider the combustion mechanism of a propellant formulation containing FBEM grains. The FBEM grains are assumed to be of spherical form of diameter d and have the burning rate of their own U_{FBEM} superior to that of the base-line propellant (U_p), and distributed in the propellant bulk as shown in Fig 7.

The time of combustion (τ) of a unit volume l^3 can be defined by

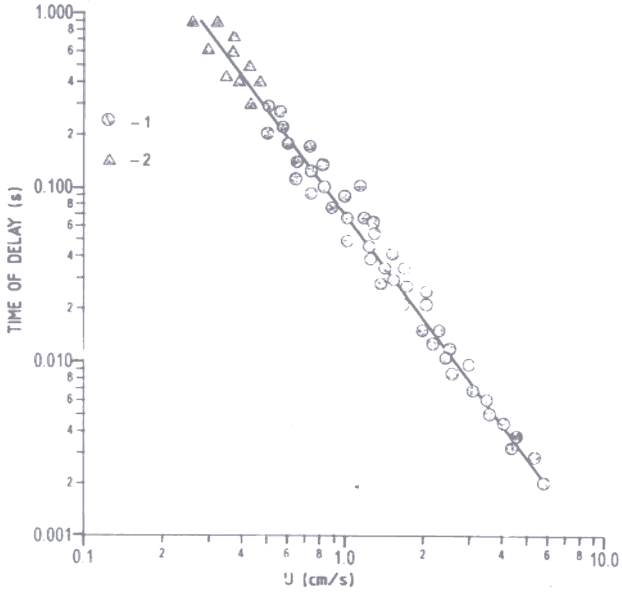

Figure 8. Ignition delay time as a function of the burning rate of AP-based composite propellants (1), and double-base propellants (2).

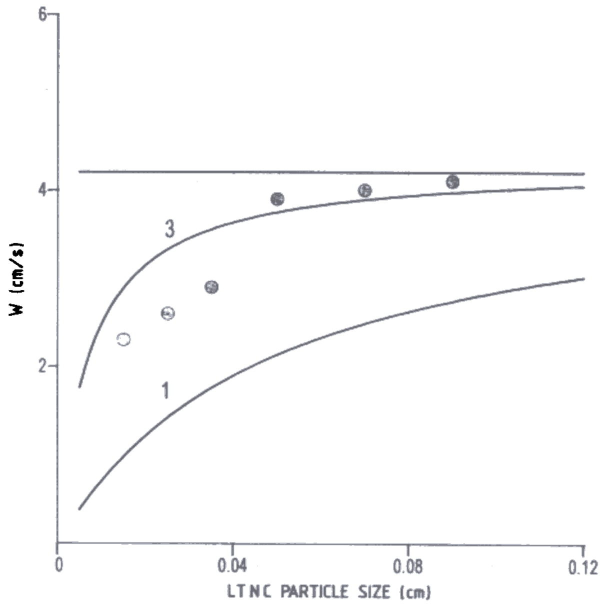

Figure 9. Experimental and calculated burning rates of a composite propellant containing 15 per cent LTNC grains at 4 MPa, as a function of LTNC particle size. Curves calculated from Eqn (8) for n = $7 \cdot 10^{-2}$ (1); $\tau_d = 0$ (2); n = $1 \cdot 10^{-2}$ (3).

$$\tau = \frac{l}{W} = \frac{l-d}{U_-} + \frac{d}{U_{FBEM}} + \tau_d \quad (5)$$

where l is the unit volume size, τ_d is the ignition delay time of the propellant layer beneath the FBEM grain, and W is the overall burning rate of the composition. Using the designation for volume fraction of FBEM grains in the propellant composition as $\alpha = d^3/l^3$ and representing the ratio of U_p/U_{FBEM} by z, W can be written as

$$W = \frac{U_p}{1 - \left(1 - z - \frac{\tau_d U_p}{d}\right) \cdot \sqrt[3]{\frac{6}{\pi}\alpha}} \quad (6)$$

It follows from Eqn (6) that $W = U_p$ at $z \rightarrow 1$ and $\tau_d \rightarrow 0$.

Ignition delay time, τ_d, has been measured for various propellant compositions burning at 1.8 to 6.6 cm/s at 10 MPa. FBEM inclusions used in the compositions had intrinsic burning rates of 22-100 cm/s at 10 MPa. Experiments carried out in the pressure range 1-20 MPa have shown that τ_d depends only on the burning rate of the starting propellant and is independent of its particular composition as well as FBEM chemical nature (Fig. 8). Experimental data for both AP-based composite propellants and conventional double-base propellants fall on a straight line, that gives an expression for τ_d:

$$\tau'_d = \frac{n}{r-2} \quad (7)$$

where n = 7.10^{-2}.

The substitution of τ_d into Eqn (6) yields the final equation for the burning rate of a propellant formulation containing FBEM grains as

$$W = \frac{U_p}{1 - \left(1 - z - \frac{n}{dU_p}\right) \sqrt[3]{\frac{6}{\pi}\alpha}} \quad (8)$$

Calculations of W from Eqn (8), using n = 7.10^{-2}, give results well below experimental data (Fig. 9, curve 1). If τ_d is not considered at all, the calculated values of W prove to be superior to experimental ones and is independent of the FBEM

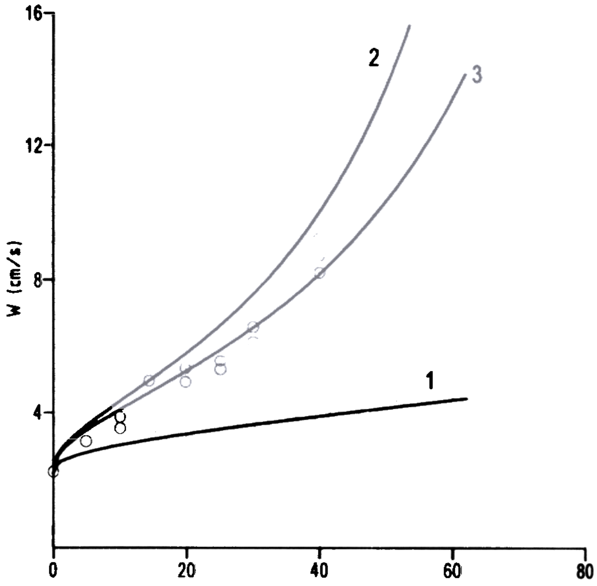

Figure 10. Experimental and calculated burning rates of a composite propellant containing LTNC of 800 μm particle size at 10 MPa, as a function of LTNC content. Curves calculated from Eqn (8) for n = 7·10^{-2} (1); τ_d = 0 (2); n = 1 10^{-2} (3).

grain size (curve 2). Experimental data may be adequately approximated by Eqn (8), if one assumes $n = 1.10^{-2}$ (curve 3).

Figure 10 demonstrates a good agreement between experimental and calculated (n = 1 10^{-2}) burning rate data for combustion of a propellant composition at different contents of FBEM grains in the formulation.

Using Eqn (8), one may derive an expression for the criterion for FBEM performance (K_p) in the propellant composition as

$$K \quad \frac{dU_p(1-z)}{10^{-}} > \tag{9}$$

When $K_p \leq 1$, FBEM additive will not increase the burning rate of the U_p, however great the FBEM burning rate level and content in the composition. The less the burning rate of the U_p, the more hard is it to accelerate by using FBEM grains.

Sometimes, when measuring the burning rate, the values obtained prove to be ten and more times greater than those for the base-line propellant. However, the combustion model proposed allows predicting the maximal burning rate of a composition with fast-burning inclusions, that is when $\alpha \rightarrow \pi/6$ and $U_{FBEM} \rightarrow \infty$.

$$W_{max} = \frac{l}{\tau_d} = \frac{dU_p^2}{0.01} \tag{10}$$

Consequently, one may assume combustion process to be unstable, if an experimental burning rate value (W) exceeds W_{max}, and define the criterion for combustion stability as

$$K_s = \frac{W}{W_{max}} = \frac{0.01\,W}{dU_p^2} \tag{11}$$

The combustion process is considered to be unstable, when $K_s \geq 1$.

Experimental data[6] on combustion of a number of individual FBEM reveal different types of pressure dependence of the burning rate; it may increase, remain constant, or decrease with increasing pressure. A guess has arisen as to use FBEM for the purpose of not only increasing the propellant burning rate but modifying burning

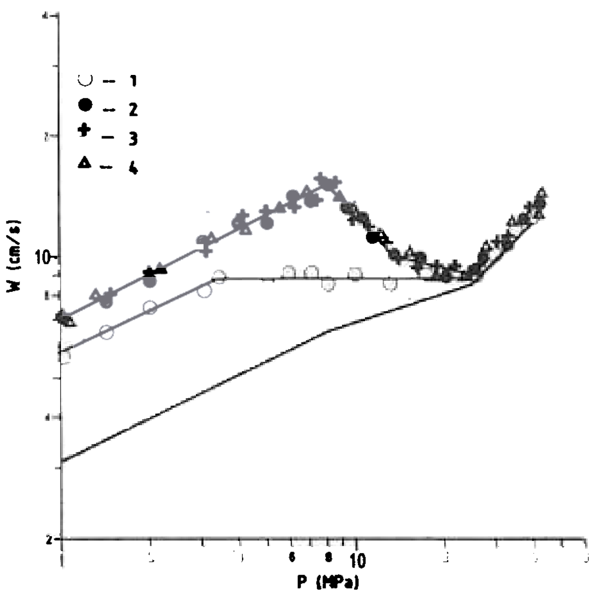

Figure 11. Effect of pressure on the burning rate of a composite propellant containing 15 per cent GP grains. GP particle size: < 400 μm (1), 400-800 μm (2), 800-1000 μm (3), 1000-1250 μm (4). Solid line without points: base-line propellant.

rate-pressure dependence as well. On experimental study, the GP has been chosen as a representative of FBEM of this type. GP is capable of giving a negative pressure exponent in the wide pressure range (10-22 MPa). Incorporation of 15 per cent GP grains into the composition burning at 6.6 cm/s at 10 MPa makes it possible to modify burning rate-pressure, rate characteristics of the propellant composition, altering the pressure exponent down up to negative values (Fig. 11).

Thus, granulated FBEM, in common with regular combustion catalysts, can be considered as universal additives capable of modifying ballistic properties of propellant compositions .

REFERENCES

1. Caveny, L.H. & Pittman, C.U. (Jr.) Contribution of solid phase heat release to ammonium perchlorate composite propellant burning rate. *AIAA Journal*, 1968, **6** (8), 1461-67.
2. Kawamura, Kazuro. Influence of copper oxide catalysts on the burning rate of a composite propellant. *J. Indus Explo Soc. Japan*, 1989, **50** (5), 415-24.
3. Robson, J.H. Composite polysulshide propellants containing additives for producing extremely fast burning. USA Patent 3, 276, 926. 8 January 1953. 2p.
4. Matsubara, H. Methods of producing propellant grain adapted for single stage rockets. USA Patent 3, 300, 549. 13 April 1964. 5 p.
5. Matsubara, H. Feststofflreibsatz und Verfahren zu dessen Merstellund. German Patent 1, 287, 493. 1 October 1963. 8 p.
6. Fogelzang, A.E., *et al.* FLAME: Database on Combustion of Explosives and Propellants. *Version* 2.50. Moscow, Russia, 1996.
7. Leibenzon, L.S. Natural liquid and gas flows in porous medium. Gostoptekhizdat, Moscow, 1947 (in Russian).
8. Zel'dovich, Ya. B. Theory of steady-state flame propagation limit. *Zhurnal Experimentalnoi Teoreticheskoi Fiziki,* 1941, **11**, 159-69 (in Russian).

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