Combustion Mechanisms of Nitramine-Based Propellants with Additives

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Propellants containing HMX and an energetic binder have a very pressure sensitive burning rate law. Modifications of the burning rate and of the pressure exponent may be obtained by adding lead salts or ammonium perchlorate (AP) to the propellant. In the first case, the additive effect is related to the possibility for the binder to produce efficient finely divided carbon near the combustion surface. In the second case, the effect results from an interaction between AP flame oxygen and binder flame products. This interaction is observed between 20 and 300 bars. Its importance depends on the AP particle size. In parallel with this experimental study, an interpretative combustion model has been developed. This model is based on a sequential combustion concept and allows one to correlate the experimental results and especially the dependence of the burning rate on the HMX mass ratio.

Nomenclature

A = pre-exponential factor
c_p = heat capacity
D = diameter
E = activation energy
f = mass fraction
M = mass
N_i = number of particle of size i in a unit volume
Q_c = heat balance in the condensed phase, cal/g
r_b = burning rate
V = volume
ξ = volumic fraction
ρ = specific mass
ϕ = heat flux transferred from gas to condensed phase

Subscripts

bind = relating to the binder
HMX = relating to the shock-sensitive explosive
prop = relating to the propellant
s = relating to the surface

Introduction

RESEARCH for better performance solid propellants leads to adding active compounds, such as HMX, in association with an energetic binder. An interesting formulation (in regard to performances, feasibility, and mechanical properties) may consist of a polymer plasticized with a nitric ester and of a solid (mainly HMX). For these compositions, it appears that the burning rate is quite sensitive to the pressure, which is generally a drawback in a rocket motor. The ability to adjust the burning rate and to effect the pressure exponent depends upon the knowledge of the combustion mechanism, in which the fact that each component burns by itself must be taken into account. Work has been carried out at ONERA[1] for several years on the experimental determination and on an interpretative model for the burning rate for propellants containing an energetic binder and HMX.

The modification of the burning rate results mainly from the possibility of intensifying the heat flux from the gas phase to the solid surface. This modification can be obtained, for example, by adding compounds (ballistic additives) that increase the rate of chemical reactions in the flame. A good example is the double-base, in which a small quantity of lead compounds gives an important super-rate. Since nitramine-based propellants possess, at least for the binder, a strong analogy with homogeneous propellants, it is reasonable to study the effects of these additives in these propellants.

If a smokeless exhaust is not a priority objective, another means of increasing the burning rate is to add ammonium perchlorate (AP). The AP flame reacts with the binder flame to give a diffusion flame. The resulting heat flux and the burning rate are sensitive to the AP mass fraction and particle size.

Literature Survey

Experimental Studies

In studies on the combustion of nitramine-based propellants, one must distinguish between inert and active binders. With inert binders, the combustion may be compared to that of a classical composite propellant (interactions between an oxidizer flame and combustible gases issuing from the binder pyrolysis). Additives decompose at the burning surface and leave a residue that modifies thermal conductivity, and thus intensifies the heat flux between the flame and the condensed phase. This is the physical aspect of the additive action. For active binders, besides this aspect, it is possible to add compounds that modify the chemical reactions in the binder flame. These two points of view will be considered, knowing that most of the published works that have been summarized by Fifer[2] are related to the inert binders.

For a polyester-cyclotrimethylene trinitramine (RDX) propellant, Zimmer-Galler[3] found a strong increase of the burning rate (~50%) when butyl-ferrocene is added. Unfortunately, the catalyst also increases the pressure exponent. According to the author, this result is the consequence of modifying the binder pyrolysis law or the binder-RDX interactions. Boehmer and Roberto[4] studied the effects of some catalysts on the burning rate of an hydroxy-terminated polybutadiene (HMX/HTPB) propellant. Among these compounds, one group of metallic salts (Cr, Fe, Cu) decreased the pressure exponent and increased the burning rate. Another group of organic bases (urea, nitroguanidine) increased the burning rate and the pressure exponent. Differential Scanning Calorimetry

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(DSC) experiments carried out with these additives did not show a correlation between the modifications of the decomposition temperature of HMX and the ballistic behavior of the propellant. Fifer noted that for nitramine/HTPB propellant (70% HMX), the additive [AP or tetramethylammonium nitrate (TMAN)] is more efficient if HMX particles are coated with AP. Pressurized DSC experiments showed that the melting and decomposition temperatures were significantly lower.

A special case has been described by McCarty et al.[5] With an HMX-(70%)-based propellant, if the polyether binder is replaced by a silicon binder, a very strong super-rate (×5) was observed. Correlatively with the super-rate, a fluffy texture (probably SiO_2) on the combustion surface was found.

Kubota and Hirata[6,7] added lead salts to an HMX-polyester propellant. The observed super-rate effect was attributed to the formation of a carbon texture. They concluded that this is the same process as in double-base propellants. Thus, the kind of binder (polyether or polyester) is not important.

For a double-base propellant used as an active binder (energetic potential ~900 cal/g), Sumi and Kubota[8] established that a progressive addition of HMX (between 0 and 23%) involves a diminution of the burning rate. If the propellant is catalyzed with a mixture of lead salt and carbon black, the super-rate is not as strong with the HMX compositions. The pressure exponent remains low, but it increases with the mass fraction of HMX.

Foster[9] summarized various works about the catalysis of energetic binder propellants. He confirmed the fact that the efficiency of lead compounds is diminished by the nitramine. The size of HMX particles is an important factor also. For example, large particles could reduce modifier effectiveness by decreasing the viscosity and reducing the degree of dispersion of the modifier. Besides the lead salts, metallic salts (Bi, Cu, Pd...) are also candidates as ballistic modifiers.

With the same point of view, Helmy[10] summarized a large number of articles. He obtained four categories of compounds likely to induce a ballistic effect. He observed that, with lead salts, a relation was found between the super-rate effect and the particle size: the smaller the size the more efficient the additives. The lead-carbon ratio was also found to be important. Strained ring molecules (e.g., adamantane) have an interesting potential energy because of their ability to reorganize structurally. However, when these compounds were incorporated in smokeless propellants, no significant effects were observed. Free radical compounds (e.g., azo-benzene) offer the possibility of producing free radicals easily. This favors more energetic decomposition in the condensed phase and consequently could induce super-rate effects. However, attempts to incorporate these compounds in PGA/HMX/BTTN propellants were not successful (PGA, polydiethylene glycol adipate; BTTN, butane triol trinitrate). Metallic carbonyl compounds (e.g., methyl-iron-carbonyl) are mainly used with composite propellants. With minimum smoke propellants, degradation reactions were observed during the polymerization. Despite these difficulties, Helmy observes that this avenue of research should be pursued.

Besides these studies on "classical additives," a special case is noted by Miller et al.[11] in a double-base propellant containing 40% of HMX. The burning rate can be increased when the HMX is coated with a thin film of isocyanate. This super-rate is attributed to a better adhesion between HMX and binder, hence the HMX residence time is increased at the burning surface.

From all these experimental studies, it can be concluded that, for minimum smoke, nitramine-based propellants, the only operational ballistic modifiers are the lead salts. If minimum signature is not a priority, the burning rate may be increased by adding AP to the propellant. Klöhn and Eisele[12] suggested a formulation with RDX, nitroglycerin, and a polyurethane binder. In that composition, if 20% of AP is added, the burning rate is multiplied by two, and the pressure exponent is depressed from 0.9 to 0.65.

Modeling Studies

Parallel modeling studies have been conducted to understand the combustion mechanisms. It is necessary again to distinguish between inert and active binders. For inert binder propellants, Kumar and Strand[13] adapted the Beckstead, Derr, and Price (BDP) model developed for AP propellants to a two solid phase propellant. There is no distinction between AP and HMX particles. The authors admitted a partial melting of the HMX at the burning surface and distinguished two regimes. For low pressures, the melting is limited, and the burning rate controlling reaction is the oxidizer degradation in the melting layer. For high pressures, the surface is totally covered by a melting layer in which the chemical reactions take place. To interpret the slope break of the burning rate law, the authors proposed that the discontinuity is a consequence of the propellant heterogeneity. There is a break when the thermal wave thickness (diffusivity/burning rate) is equal to the particle diameter.

Cohen and Price's model[14] for inert binder propellants is also based on the BDP approach. The difference with the Kumar-Strand model is due to a distinction between AP and HMX particles (stoichiometry, flame energy, and melting points are not the same). It is assumed that there is a total melting of HMX. The burning rate is given by taking into account the structure of the surface and of the flame in the conservation laws.

Kubota and Masamoto's model[15] assumed that an active binder propellant and a double-base propellant behave identically, particularly the gas phase reactions are the same; only the heat feedback at the surface is different and given by

$$Q_s = f_{\mathrm{HMX}} Q_{s_{\mathrm{HMX}}} + (1 - f_{\mathrm{HMX}}) Q_{s_{\mathrm{D.B.}}}$$

A model developed by Cohen and his colleagues[16,17] for active binders supposes a separated degradation for binder and for HMX. From experimental observations, it is said that the HMX is totally melted at the surface. In rocket motor conditions, the liquid-gases transition is mainly due to a vaporization (95%); consequently the heat balance in the condensed phase is endothermic. On the other hand, the chemical reactions of the binder degradation are exothermic. At low pressures, the binder burning rate is controlled by the exothermic reactions in the condensed phase and, at high pressures, by the flame reactions.

In the propellant, the combination between these two phenomena involve the melting of fine HMX particles on the burning surface. Mixing between HMX and binder significantly decreases the total exothermicity. In the flame, there is no chemical interaction between HMX and the binder, only a superposition of the heat flux. Consequently, for a low energy binder, the addition of HMX increases the burning rate of the propellant (with respect to the binder rate) and, for a high-energy binder, the burning rate decreases. If there are additives, the lower exothermicity of the condensed phase added to a thinner combustion zone for the propellant, as compared to the binder, induce poor degradation of the additives. The larger is the particle size and the higher is the combustion pressure, the worse is the additive degradation, and therefore its action.

All the previous models have adopted the concept of a combustion in parallel. At any time the interactions between each component are proportional to their volumic fraction. But if the burning rate and the surface temperature of compounds are very different, this point of view is not realistic. This is why Beckstead[18] proposed a sequential combustion concept in which the flame front runs across the binder and the HMX particles successively. The average burning rate is given by the ratio between the sum of distances and the sum of times:

$$r_b = \Sigma \text{ distances}/\Sigma \text{ times}$$

The distances successively concern the thickness of binder and of HMX. The times are the combustion times; for an *i* species it becomes

$$t_i = \text{distance}_i / r_{bi}$$

In addition to the combustion times, Beckstead considered that there is an extra time before ignition when an HMX particle arrives at the surface. For an inert binder, its pyrolysis is controlled by the heat flux coming from the oxidizer. If the burning rates of components are different, there are discontinuities in the heat-flux propagation, and Beckstead added a transfer time to take into account these discontinuities. In visualization experiments of the combustion, chips of binder were observed to peel off the surface without burning. This phenomenon is mainly observed for low pressures and depends upon the heat flux of the primary flame, upon the initial temperature, and upon the propellant stoichiometry. This notion, called fraction of binder reacting, is an adjustable parameter in the model.

ONERA Approach

The first point of the approach at ONERA was to study the combustion mechanisms of each propellant component using detailed experimental data. These tests, conducted with HMX, double-base binders, and energetic binders, allowed development of combustion models that account for the burning rate behavior.[1,19,20] Second, the parameters that modify the burning rate of a propellant were studied (mass fraction and particle size of HMX, ballistic additives). Finally, an interpretative model (in the same spirit as that of Beckstead) was developed. This model assumes a sequential combustion of compounds and takes into account the difference between the surface temperature of HMX and the binder. This difference implies transitory conditions in the HMX combustion. Thus, the burning rate is not just an average of the components burning rate. A delay must be added, but this extra time does not have the same significance as the delay time in Beckstead's model. The last point was to study the influence of AP over a very large range of pressures.

Experimental Results

HMX

The kinetics of the HMX degradation, in the condensed phase, were determined by DSC and confirmed by ignition tests. For a given reaction order ($n = 1$), the Arrhenius parameters are $A = 1.1\ 10^{17}\ \text{s}^{-1}$ and $E = 50$ kcal/mole. Microthermocouples embedded in HMX allowed the confirmation of the validity of this kinetic law under burning conditions. It is not obvious a priori that DSC (slow heating rates) degradation kinetics and combustion degradation kinetics (very high heating rates) should be the same. It is felt that, in the case of HMX, this agreement is verified.[1] The same conclusion was reached for double-base propellants.[19] From the microthermocouple tests, it was also deduced that the HMX degradation in the condensed phase is globally exothermic. Molten HMX has been observed in various studies on nitramines[21-24] and on the surface of propellants using fine HMX and an inert binder.[25] In this case (energetic binder), no evidence confirming the existence of an important HMX melting layer was observed. The tests and the interpretation are described in detail in Ref. 1. The pyrolysis gases were sampled and analyzed by mass spectrometry. The main species are nitrogen oxides (NO_2, NO, N_2O: ~60%), aldehydes and hydrogen cyanide (~30%).[26] As in a double-base propellant flame, the HMX flame is a two-stage flame (see Fig. 1), but the separation was observed only for very low pressures. For pressures above 10 bars, the two flames are merged.

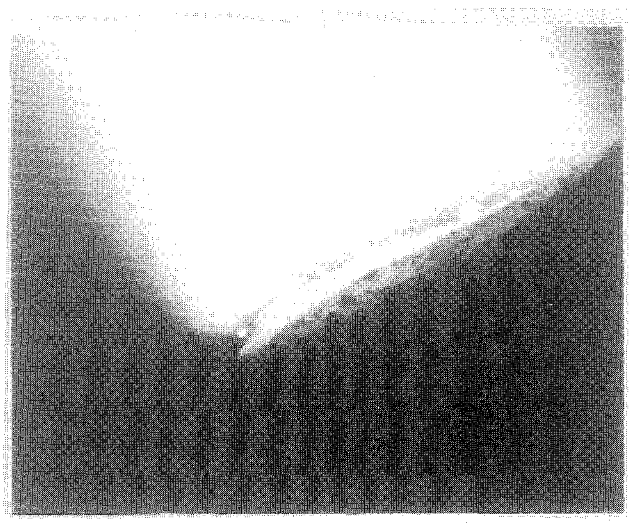

Fig. 1 HMX flame ($P = 1.5$ bars).

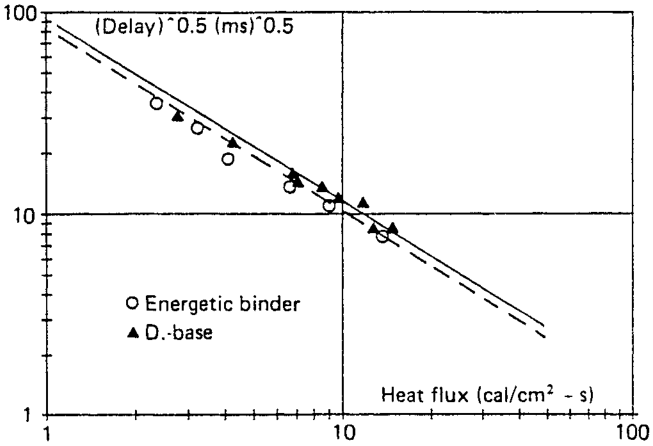

Fig. 2 Comparative ignition law.

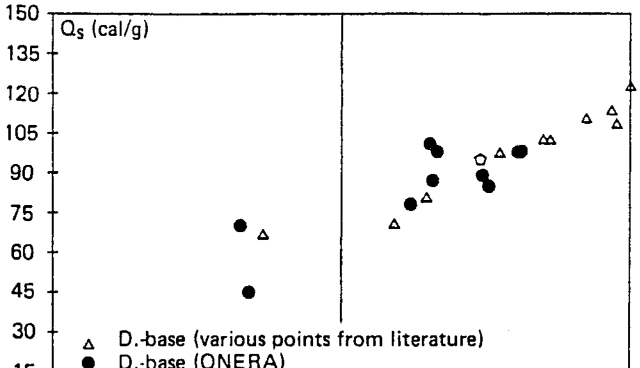

Fig. 3 Heat released in the condensed phase.

Energetic Binder

In this work, the binder is a polymer (polyester or polyether) plasticized by nitroglycerin. The heat of explosion is about 800 cal/g. The choice of the kind of polymer has a consequential effect on the burning rate, especially if it is a catalyzed composition.

The same method (DSC) was applied to the binder. A value of 38 kcal/mole was found for the activation energy.[27] This value is nearly equal to the value generally adopted (40 kcal/mole) for the double-base propellants.[19] Ignition tests again confirmed the value of the kinetic parameters. In Fig. 2, the ignition laws of a double base and of an energetic binder are presented. Note that the slope of the curves is identical. The difference in magnitude is due only to the different thermal effusivities. From these results, it was deduced that the binder pyrolysis is the same as that of double-base propellants.

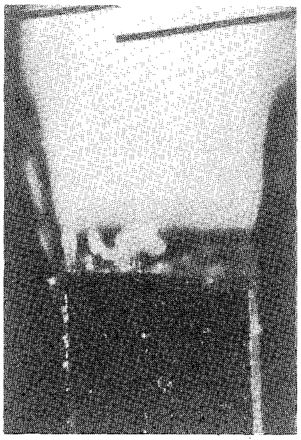

Fig. 4 Energetic binder flame.

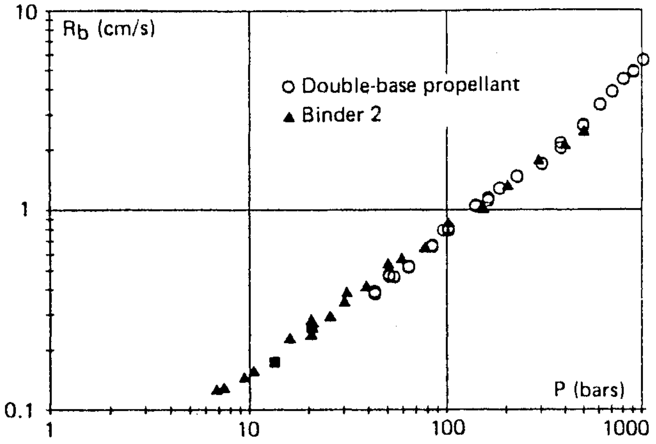

Fig. 5 Comparative burning rate law.

From the analysis of thermal profiles, it was possible to evaluate the energetic balance in the condensed phase. An example reported in Fig. 3 confirms the analogy with double-base propellants. This analogy was also confirmed by combustion visualization tests. An example of the two-stage flame is reported in Fig. 4. In contrast to the HMX flame, the separated flames are maintained for high pressures (~100–200 bars). Because the NO_2 mass fraction and the heat of explosion are the same for both propellants, it is only natural[17,28] that the burning rates are identical (see Fig. 5). (It has been noted by one reviewer that the identity between energetic binder and double-base propellant might not be systematic. In our case, it could be due to the use of the same plasticizer.)

Propellant

The effects of adding HMX in the propellant were studied and the influence of the particle size considered. Figure 6 compares the burning rate law for a propellant containing 70% of HMX to the burning rate of the binder and of HMX. Two combustion regimes are very clearly observed. For low pressures (< 100 bars), the burning rates of the propellant and of the binder are merged (the pressure exponent is about 0.7). For high pressures (>200 bars), the propellant burning rate increases drastically (the pressure exponent is about 0.9) with a tendency to approach the HMX burning rate.

Except for high pressures (>200 bars), the HMX mass fraction (between 30 and 70%) (see Fig. 7) and the HMX particle size (see Fig. 8) had no effect.

Effects of Additives

Tests were conducted with two kinds of binder (noted as 1 and 2) and with the corresponding propellants. The differences were the kind of polymer and of nitric ester. The mass fraction of HMX was 70% in the propellant. The ballistic additives

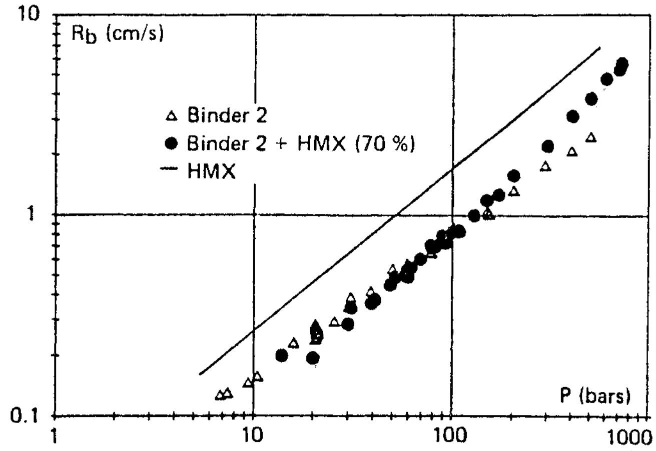

Fig. 6 Experimental burning rate of an HMX-based propellant.

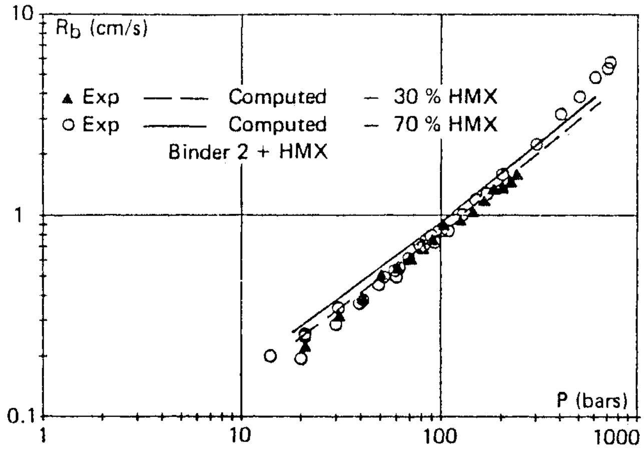

Fig. 7 Influence of the HMX mass fraction.

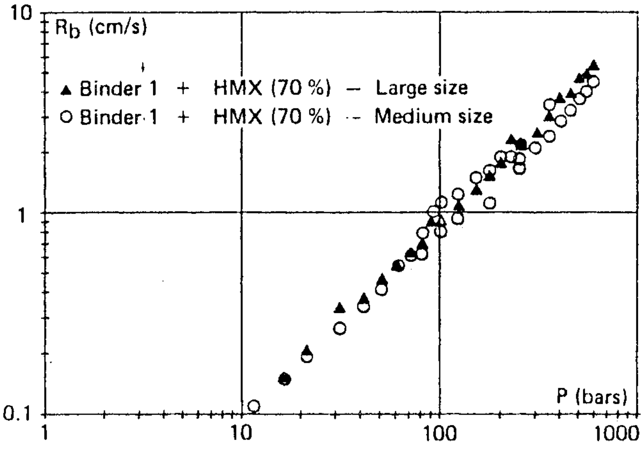

Fig. 8 Influence of the HMX particle size.

were a mixture of lead salt and of carbon black. The ratio additives/binder was the same in the binder alone and in the propellant.

For binder 2 alone, carbon black is an important factor; it increases the super-rate effect and the pressure range where the additives act (see Fig. 9). With binder 1—the heat of explosion of which is about 730 cal/g against 800 cal/g for binder 2—the same effects are observed (see Fig. 10). Nevertheless, the super-rate effect with lead salt and carbon black is more important in the case of binder 2 for pressures below 100 bars.

In the propellant with binder 2, the effects of additives are drastically diminished (see Fig. 11). In contrast, with binder 1, the effects of HMX are to increase the burning rate (see Fig. 12). To interpret these results, it is possible to refer to homogeneous propellants.[29] In such compositions, the pyrolysis of the condensed phase (breaking of the -O-NO_2 bonds) produces mainly NO_2 and aldehydes, which react in the primary flame. At the same time, the nitrocellulose degradation gives a microscopic carbon structure on the burning surface. The additives are trapped in this structure and have time to react with aldehydes to produce extra carbon, which reacts with NO in the primary flame. The heat release is intensified and the burning rate increased. If carbon black is added, the phenomenon is amplified. In this process, the basic fact is the ability for the binder to form a very efficient carbon structure. This structure of carbon deposit must stay on the propellant surface, and its size must be comparable with the primary flame thickness.

The pyrolysis law is the same for the two binders and for a double-base propellant. The quantity of available carbon (for an equivalent heat of explosion) is also identical. Since the gaseous species that react in the primary flame are about the same, the burning rate must be about the same. This behavior is true for compositions without additives (see Fig. 5) but not if there are additives (see Figs. 9 and 10). It is believed that the differences are due to the ability for the different polymers to give an efficient structure. Reference 1 reports the structures obtained under combustion conditions with a double-base propellant and with binders 1 and 2 (without additives). The structure of binder 2 is rougher than the double-base structure, but practically no structure is created with binder 1. If additives are incorporated in binders 1 and 2, the carbon structures created during the combustion differ significantly. With binder 2, the carbon is very powdery (see Fig. 14) with a great possibility to react in the primary flame. On the other hand, the carbon from binder 1 is stratified and the carbon layers peel off the surface before reaction (see Fig. 13).

In the propellant (with HMX), the additives are more effective with binder 1 than with binder 2 (see Figs. 11 and 12). To explain this fact, it is assumed that the HMX combustion has two effects on the combustion process. The first effect increases the heat flux at the surface so that there can be a better pyrolysis of the polymer fraction of the binder and probably the production of a finer carbon structure. The second effect decreases the burning rate because the additives are effective only with the binder fraction of the propellant, and the 70% HMX dilutes the total amount of carbon structure. The average burning rate is a resultant of the preponderance of either of these factors. By comparing the results of a binder 2-additives mixture to those of a catalyzed double-base propellant, it is seen that the maximum super-rate is already obtained before introducing HMX (see Fig. 9). Hence, only a negative effect can occur when introducing HMX. On the other hand, the

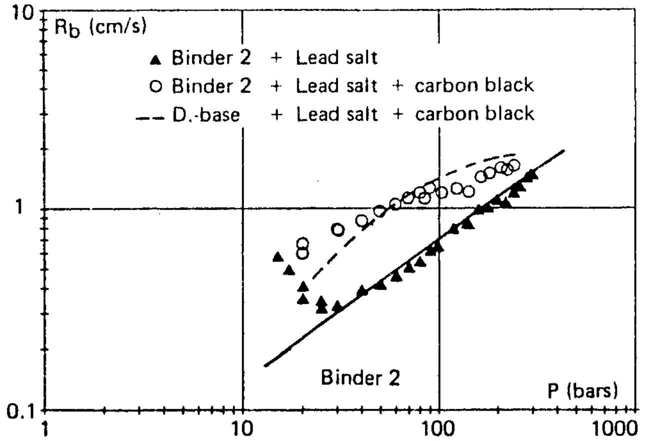

Fig. 9 Effect of additives on binder 2.

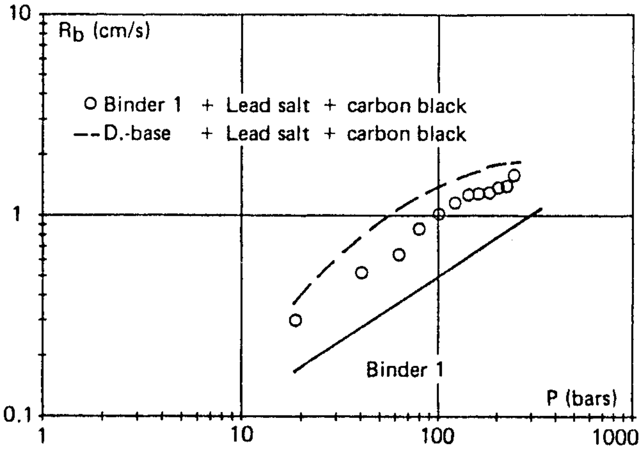

Fig. 10 Effect of additives on binder 1.

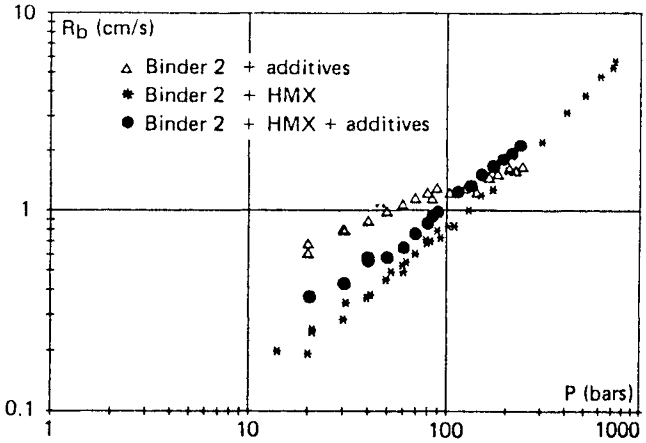

Fig. 11 Effect of additives on propellant.

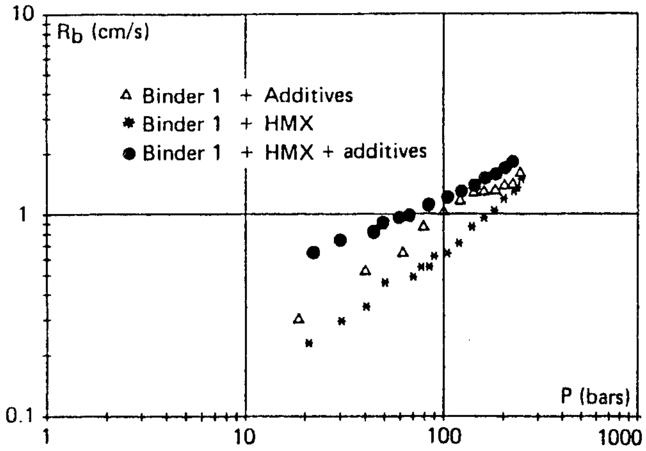

Fig. 12 Effect of additives on propellant.

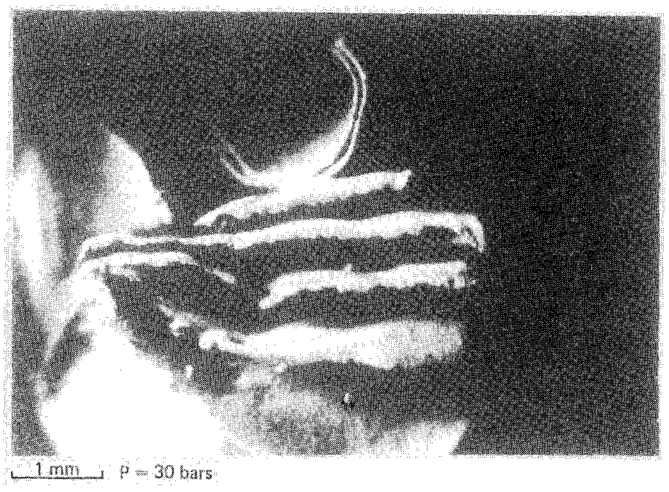

Fig. 13 Carbon structure from binder 1 + additives.

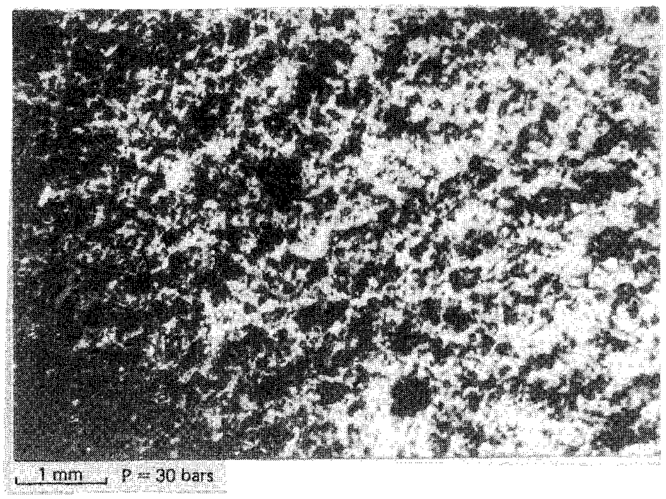

Fig. 14 Carbon structure from binder 2 + additives.

energetic contribution of HMX induces a better degradation of the polymer, and a positive effect is predominant with the binder 1-additives mixture.

Influence of AP

Using AP as a ballistic modifier is a special case of the work aiming at modifying the burning rate of nitramine-based propellants when a smokeless exhaust is not required. The AP mass fraction in the propellant is generally more important than the mass fraction of classical additives. The AP flame reacts with the species issuing from the binder pyrolysis. So great are these interferences that the classical additives are no longer effective.

Apart from these restrictions, AP addition increases the burning rate very significantly.[1,12] The burning rate depends upon the AP mass fraction, and moreover, for a same mass fraction, the burning rate and the pressure exponent depend upon the AP particle size (see Fig. 15). This sensitivity of the pressure exponent to the particle size (already observed with composite propellants) corresponds to the fact that the combustion is controlled by a diffusion flame between oxidizing gases (from the AP combustion) and combustible gases (from the binder pyrolysis). Nevertheless, this combustion mode takes place in a limited pressure range (between approximately 10 and 300 bars). At lower and higher pressures, the premixed flame mode controls the combustion (the pressure exponent does not depend upon the particle size). These different modes are believed to be related to the nature of the AP and binder flames. For low pressures, the interaction between the AP flame and the binder primary flame is kinetically controlled. For high pressures, the secondary flame of the binder is close to the surface and the chemical reactions (of this flame) take place before any reaction with the oxidizing gases from AP. Of course, the pressure where the various combustion regimes occur depends upon the particle size. The smaller the particle, the higher the threshold pressure. Fortunately, for rocket motor applications, the diffusion controlled process takes place in an interesting pressure range.

Combustion Mechanism Interpretation

Model

In this work only the compositions containing HMX and binder (with or without additives) are considered, which excludes propellants containing AP. As noted previously, Beckstead's concept[18] of a sequential flame has been adopted; the binder and HMX burn separately without chemical interactions. This concept is based on the scanning electron microscope observations, which show no evidence of sufficient melting of the HMX and energetic binder to the point that they totally melt together and premix at the surface as hypothesized by Cohen et al.[16] The differences with Beckstead's model are because the transfer delay and the notion of reacting binder fraction that he takes into account are not applicable to an energetic binder. Moreover, the delay related to HMX (ignition delay for Beckstead) has a different significance. This point will be studied later. In these conditions, the basic burning rate equation is given by

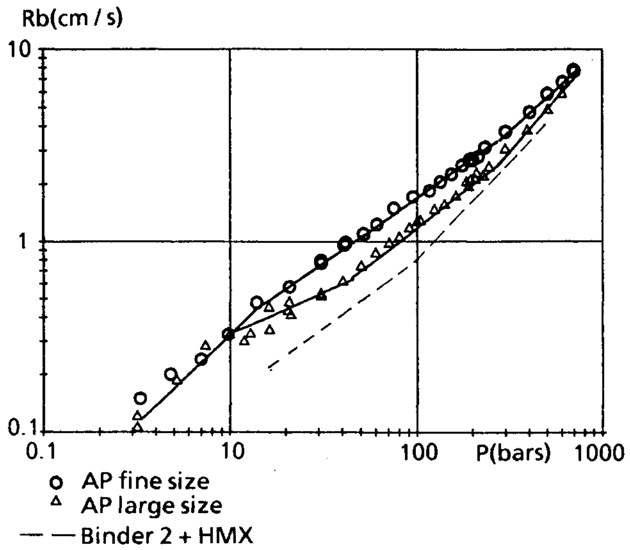

Fig. 15 Influence of ammonium perchlorate (binder 2-HMX-AP).

$$r_b = \frac{\Sigma\ \text{distances}}{\Sigma\ \text{times}} = \frac{\Sigma\ \text{distances}}{\Sigma\left(\dfrac{\text{distances}}{r_b} + \text{delay}\right)} \tag{1}$$

If an ideal distribution for the components is admitted, each HMX particle is surrounded by a binder layer, the thickness (Δ) of which is determined by the propellant formulation

$$\xi = \frac{V_{\text{HMX}}}{V_{\text{prop}}} = \frac{(D_{\text{HMX}})^3}{(D_{\text{HMX}} + 2\Delta)^3} \tag{2}$$

The volumic fraction ξ can be related to the mass loading ratio with

$$f = \frac{M_{\text{HMX}}}{M_{\text{prop}}} = \frac{V_{\text{HMX}}\rho_{\text{HMX}}}{V_{\text{prop}}\rho_{\text{prop}}} = \xi\,\frac{\rho_{\text{HMX}}}{\rho_{\text{prop}}} \tag{3}$$

The propellant volumic mass is given by the equation

$$\rho_{\text{prop}} = \frac{\rho_{\text{bind}}\rho_{\text{HMX}}}{\rho_{\text{HMX}}(1-f) + \rho_{\text{bind}}f} \tag{4}$$

Associating Eqs. (2) and (3) yields

$$\frac{D_{\text{HMX}}}{D_{\text{HMX}} + 2\Delta} = \left(f\,\frac{\rho_{\text{prop}}}{\rho_{\text{HMX}}}\right)^{1/3} \tag{5}$$

Hermance[30] has shown statistically that the average intersection diameter of a plane through a group of particles is given by the relation

$$D' = D\left(\frac{2}{3}\right)^{1/2} \tag{6}$$

For an HMX particle surrounded by a binder layer (of thickness Δ),

$$D + 2\Delta = D' + 2\Delta' \tag{7}$$

This equation gives the average crossing distance for an HMX or a binder thickness. Equation (5) can be expressed as

$$\frac{D'+2\Delta'}{D'} = 1 + \frac{2\Delta'}{D'} = \left(\frac{3}{2}\right)^{1/2}\left(f\frac{\rho_{\text{prop}}}{\rho_{\text{HMX}}}\right)^{-1/3} = B \tag{8}$$

Equation (1) can be written if the totality of particles (per unit volume) is considered:

$$r_b = \frac{\Sigma N_i(D_i'+2\Delta_i')}{\left[\Sigma N_i\left(\dfrac{D_i'}{r_{b_{\text{HMX}}}} + \Delta t_i + 2\dfrac{\Delta_i'}{r_{\text{bind}}}\right)\right]}$$

$$r_b = \frac{\Sigma N_i D_i'\left(1+\dfrac{2\Delta_i'}{D_i'}\right)}{\left[N_i D_i'\left(\dfrac{1}{r_{b_{\text{HMX}}}} + \dfrac{\Delta t_i}{D_i'} + \dfrac{2\Delta_i'}{D_i' r_{b_{\text{bind}}}}\right)\right]} \tag{9}$$

For a single size, Eq. (9) can be simplified:

$$r_b = \frac{\left(1+\dfrac{2\Delta'}{D'}\right)}{\dfrac{1}{r_{b_{\text{HMX}}}} + \dfrac{\Delta t}{D'} + \dfrac{2\Delta'}{D' r_{b_{\text{bind}}}}}$$

In combining with Eq. (8),

$$r_b = r_{b_{\text{bind}}}\frac{B}{\dfrac{r_{b_{\text{bind}}}}{r_{b_{\text{HMX}}}} + B - 1 + r_{b_{\text{bind}}}\dfrac{\Delta t}{D'}} \tag{10}$$

Now in Eq. (10), only the delay must be determined. Beckstead considered that this extra time represents the HMX ignition delay. He admitted that the particle arriving at the combustion surface is not modified by the thermal profile in the propellant. In our case, the thermal profile thickness ($e_p \sim (\ell n\, 10)\, \mathrm{d}p/r_{b_{\text{bind}}}$) varies between about 130 and 20 μm over the large range of pressure (20–300 bars). This thickness is either larger than the HMX average diameter or approximately the same. So it is possible to postulate that when the HMX particle is level with the surface, it has the same temperature as the binder surface. This surface temperature corresponds roughly to the first HMX ignition temperature[20] (the beginning of degradation reactions). The delay to be taken into account is, in this case, a transition delay during which the HMX particle temperature increases from the binder-surface temperature to its own surface temperature in the established combustion regime. For example, at 20 bars, $T_{s_{\text{bind}}}$ is about 610 K and $T_{s_{\text{HMX}}}$ is about 830 K. While this transition delay occurs, it may be considered that the HMX particle receives the average heat flux between the binder flux and the HMX flux

$$\phi = (\phi_{\text{bind}} + \phi_{\text{HMX}})/2 \tag{11}$$

with $\phi_i = \rho_i Q_{c_i} r_{b_i}$; this equation expresses that each flux drives the regression of the corresponding component.

Then, the delay can be estimated if it is said that this flux is responsible for the ignition-established regime transition. This leads to

$$\rho_{\text{HMX}} c_{p_{\text{HMX}}} \frac{\mathrm{d}T}{\mathrm{d}t}\frac{4}{3}\Pi\left(\frac{D_{\text{HMX}}}{2}\right)^3 = \phi 4\Pi\left(\frac{D_{\text{HMX}}}{2}\right)^2 \tag{12}$$

$$\Delta t = \rho_{\text{HMX}} c_{p_{\text{HMX}}}\left(T_{s_{\text{HMX}}} - T_{s_{\text{bind}}}\right)\frac{1}{6}\frac{D_{\text{HMX}}}{\phi} \tag{13}$$

Equation (12) indicates that the flux is related to the exposed surface during the transition time. If the burning rate is computed from Eq. (10) (at $P = 20$ bars, for example), it is found that the delay must be equal to 1 ms to correlate the experimental data. Then it is possible to determine the burned binder thickness during this time. This computation indicates, for different HMX sizes, that the average thickness is about half the particle diameter. So it is justified to consider an effective flux lower than the one determined from Eq. (11):

$$\phi_{\text{eff}} = \frac{\phi}{2} \tag{14}$$

Equation (10) becomes

$$r_b = \frac{B r_{b_{\text{bind}}}}{\dfrac{r_{b_{\text{bind}}}}{r_{b_{\text{HMX}}}} + B - 1 + \dfrac{r_{b_{\text{bind}}}\rho_{\text{HMX}} c_{p_{\text{HMX}}}(T_{s_{\text{HMX}}} - T_{s_{\text{bind}}})}{(2/3)^{1/2} 6\phi_{\text{eff}}}} \tag{15}$$

B is given by Eq. (8). From Eq. (15), it is possible to note that the HMX particle size does not affect the burning rate. This equation sums up the model.

To simplify the computations, the experimental burning rate data for the binder and HMX are introduced in the model for the propellant. It would also be possible to obtain them from the modeling developed for HMX combustion[1] and for binder combustion.[20]

Model Evaluation

First, the influence of the transition delay was determined. Figure 16 shows burning rate data for one given propellant along with the burning rate computed with and without the delay. Between 20 and 300 bars, a good agreement is obtained if the delay is included. For higher pressures, the delay is

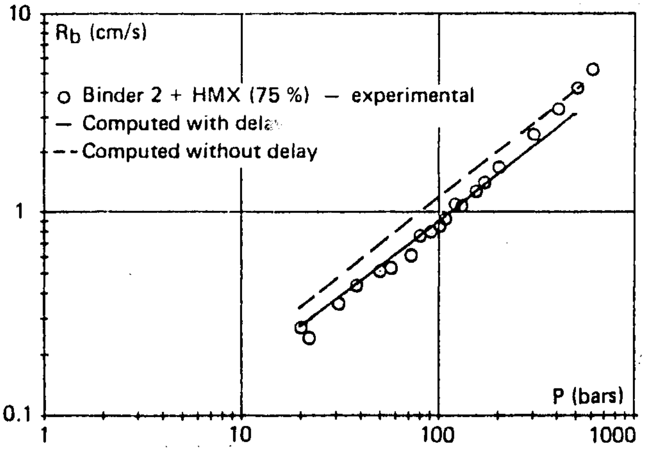

Fig. 16 Influence of the transition time.

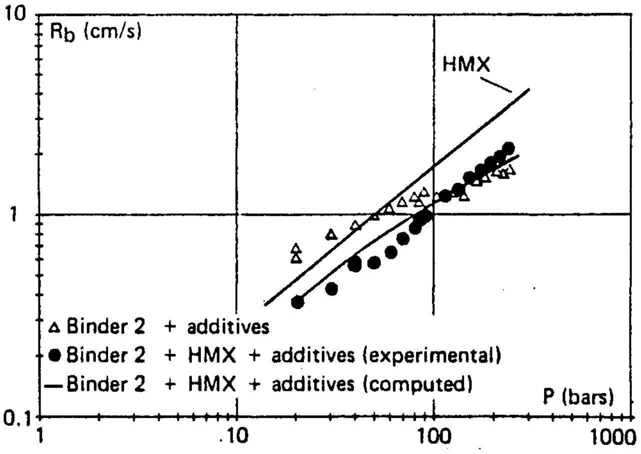

Fig. 17 Comparison between experimental and computed values.

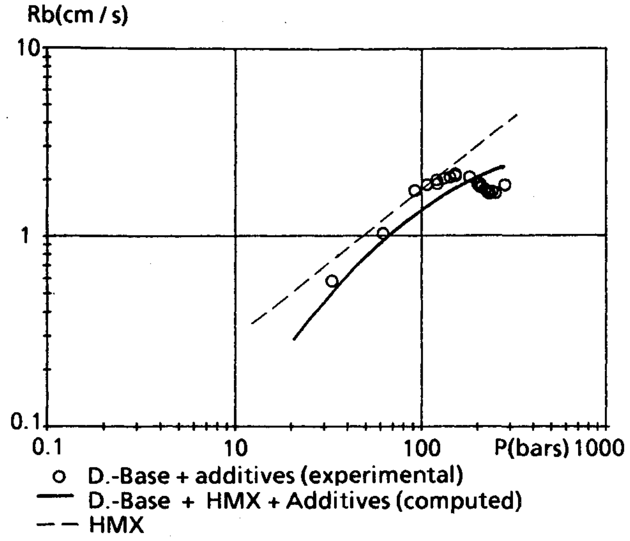

Fig. 18 Burning rate simulation for an HMX-based propellant with a double-base binder.

over-evaluated, and hence the effective heat flux must be reconsidered.

The insensitivity of the burning rate to HMX particle size is included in Eq. (15), and the experimental results shown in Fig. 8 for two different sizes agree with the model. Also, the HMX mass fraction, between 30 and 70%, has very little influence on the burning rate (see Fig. 7). However, it must be noted that the effect of this parameter depends on the binder burning rate. For a binder with a burning rate different from that of Fig. 7, one would establish more important variations with the mass fraction of HMX in the corresponding propellant.

The model has also been applied to a formulation with additives (binder 2 + lead salt + carbon black). The agreement with experimental data (see Fig. 17) is adequate. Nevertheless, it is clear that without any modification of the entry parameters, the model cannot correlate the results of Fig. 12 related to binder 1. It is assumed that, in the presence of HMX, the binder pyrolysis is more complete, the carbon has a finer structure, and therefore the action of the additives is more pronounced. In this case, the combustion model for the propellant should account for a stronger super-rate in the binder burning rate. Additional work is required to verify this hypothesis.

One of the interesting aspects of the model is to evaluate the binder burning rate which is necessary to obtain the expected value for a desired propellant burning rate. Figure 18 presents a hypothetical (to the extent that the active binders under consideration cannot be modified by additives as strongly as in the case of a double-base propellant) result with a double-base binder (with additives) containing 70% of HMX. With these conditions, it would be possible to obtain a burning rate close to 20 mm/s and a low pressure exponent between 100 and 200 bars.

Conclusions

The experimental work has shown that it is possible to modify the burning rate and the pressure exponent of a propellant containing HMX and an energetic binder by adding a lead salt and carbon black. The effect of the additives is related to the ability of the binder to give a fine carbon texture. The addition of AP to the propellant (with no other additive) enables the control of the burning rate and the pressure exponent. This control results from an interaction between the AP and binder flames. The burning rate and the pressure exponent are then sensitive to the AP particle size.

An interpretative model of the combustion has been developed. This model contains the influence of the main parameters controlling the burning rate. There is a fair agreement between computed and experimental data. It should be noted that the agreement is for burning rate levels only. Further work should be conducted to check whether proper values of the pressure exponent and of the temperature sensitivity are obtained.

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