Solid propellant combustion mechanisms and flame structure

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Abstract

AP and HMX are the two oxidizers used most often in modern solid propellants, either composite propellants or composite modified double base propellants. Although the two oxidizers have very similar combustion characteristics as monopropellants, they lead to significantly different characteristics when combined with binders to form propellants. Also, different characteristics result depending on the particular binder system used. This paper discusses various flame structures and mechanisms that apparently lead to these similarities and differences, with emphasis on the qualitative effects of flame structure on combustion mechanisms.

For AP composite propellants, the primary flame is more energetic than the monopropellant flame, leading to an increase in burn rate over the monopropellant rate. This also leads to a very strong particle size dependence. In contrast the HMX primary flame is less energetic than the HMX monopropellant flame and ultimately leads to a propellant rate significantly less than the monopropellant rate in composite propellants. In HMX composite propellants the primary flame apparently robs energy from the monopropellant flame leading to a reduced rate with little particle size dependence. In double base propellants HMX has little effect on the burning rate.

INTRODUCTION

The two oxidizers used most often in modern solid propellants are ammonium perchlorate, AP, and HMX (or RDX). AN (ammonium nitrate) is a third oxidizer that has been used on a limited basis, but studying its combustion characteristics can give insight to combustion mechanisms in general. The two most common binder systems consist of either an inert binder system based on a polybutadiene polymer, HTPB, with various plasticizers, additives and cross linking agents or an active binder system based on energetic components such as nitroglycerin, NG, and nitrocellulose, NC. In general, comparing the combustion characteristics of monopropellants with the characteristics that occur when the monopropellants are combined with other ingredients to form propellants leads to an understanding of the physical mechanisms that are involved. This paper discusses the characteristics of the monopropellants and the propellants and then conjectures the importance of the various mechanisms involved. The emphasis is on the qualitative effects of flame structure on combustion mechanisms. Time will not allow a detailed examination of the quantitative aspects of flame structure, indeed the entire symposium is dedicated to the subject. For the same reasons, consideration of combustion characteristics has focused on temperature profiles and on burning rate characteristics. Temperature sensitivity, erosive burning, ignition or unstable combustion are beyond the scope of that considered here.

MONOPROPELLANT AND COMPOSITE PROPELLANT BURNING CHARACTERISTICS

The relative burning rates of HMX, AP, and AN as monopropellants and in composite propellant mixtures are shown in Fig. 1. As monopropellants the rate of HMX is slightly higher than that of AP and both are significantly higher than that of AN. All three have very comparable burn rate exponents (for typical solid propellant rocket pressures). The adiabatic flame temperatures are very different; for HMX ~3200 K; for AP ~1400 K; and for AN ~1247 K.
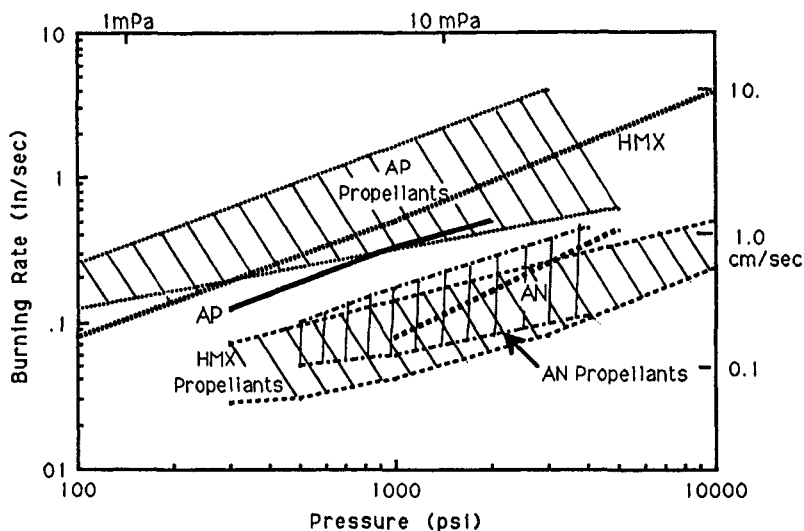
Fig. 1. Burning rate characteristics of composite propellants.

Although AP and HMX have very different flame temperatures, they have very similar combustion characteristics. This is apparently due to a higher reactivity of the chlorine oxides (the surface products from the condensed phase) of the AP compared to the nitrogen oxides (i.e. the typical surface products) of HMX. This observation is supported by the much lower rate of AN which has a flame temperature comparable to AP but does not give off the reactive chlorine oxides. The decomposition products from AN are more comparable to those of HMX, and one would expect similar reaction kinetics to be involved with AN and HMX, but not with AP. Therefore, the much lower rate of AN would correspond to the much lower flame temperature of AN compared to that of HMX.

AP and HMX appear to have similar monopropellant combustion characteristics, but when mixed with a fuel binder into a composite propellant, the resultant burn rates vary by as much as an order of magnitude. The burn rate of AP composite propellants exhibits a very strong particle size dependence. In contrast, the burn rates of HMX composite propellants are much lower than AP propellants, and show very little particle size dependence. Although the HMX monopropellant rate is approximately an order of magnitude greater than that of AN, both have comparable rates when mixed into composite propellants, and neither show as much particle size dependence as AP propellants.

Thermochemical calculations for AP composite propellants indicate a primary flame temperature on the order of ~2500-2800 K for typical concentrations. Thus, the AP diffusion flame is much more energetic than the AP monopropellant flame and leads to higher burning rates. HMX composite propellants have adiabatic flame temperatures on the order of 2000 K implying a less energetic diffusion flame than the monopropellant flame. Apparently the HMX diffusion flame robs energy from the monopropellant flame, suppressing the overall propellant burn rate. AN composite propellants have adiabatic flame temperatures on the order of ~1500-2000 K. The AN diffusion flame is more energetic than the AN monopropellant flame, but apparently not enough to cause a significant increase in burn rate (most likely due to the lower reactivity of nitrogen oxides compared to the chlorine oxides from AP).

Because of the very large differences in burning rate of the different composite propellants it appears that the dominant mechanism in the propellant combustion must be related to the primary diffusion flame (i.e. as opposed to the monopropellant flame). More will be said about this later.

MONOPROPELLANT AND DOUBLE BASE PROPELLANT CHARACTERISTICS

Double base propellants burn with characteristics significantly different than composite propellants. Figure 2 contains typical double base propellant burn rates which are compared to AP and HMX monopropellant burning rates. Double base propellant burn rates correlate very well with their heat of explosion (Hex); the more energetic propellants having the greater burn rates. Low energy propellants have rates lower than AP or HMX and high energy propellants
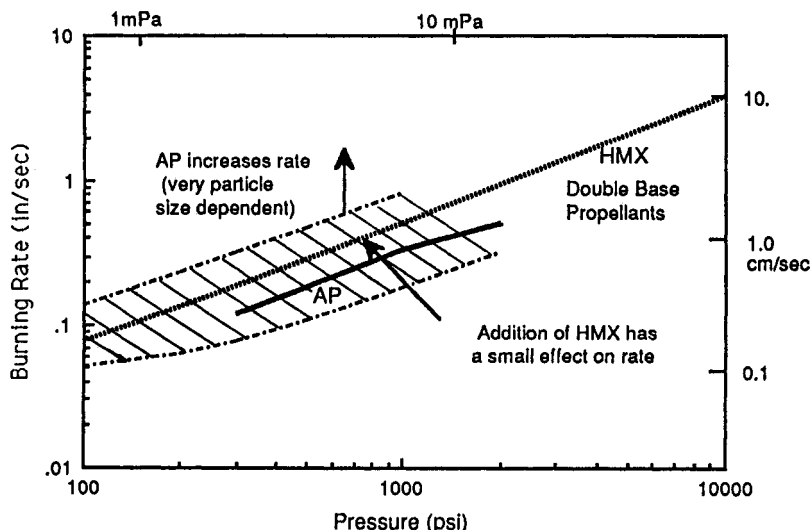
Fig. 2. Burning rate characteristics of double base propellants.

have rates greater than with AP or HMX. The energy content of HMX and double base are comparable and both contain the same elements, CHON. Thus, it is not surprising that their rates are comparable. However, a double base propellant with an energy level equivalent to HMX will have a slightly higher rate than HMX. Apparently the composition of the DB surface products is more reactive than those from HMX. A key ingredient in HMX surface products that is not present in DB products is HCN. It could be that the reaction paths associated with HCN may be related to the slightly lower reactivity of the HMX. In contrast, the lower energy content of AP gives rates comparable to either DB or HMX, apparently due to the more reactive chlorine oxides as discussed above.

Many modern double base propellants contain AP, HMX or a combination of the two oxidizers. Adding AP to a double base binder causes a significant effect on the burn rate due to the significant differences in the AP and double base chemistry. Smaller AP particle sizes cause a greater increase that larger particles. Thermochemical calculations varying the percent AP with double base binders of varying H_{ex} show that the flame temperature is a very strong function of binder H_{ex} and the percentage AP. For a low energy binder the flame temperature increases with the addition of AP, with a peak temperature occurring at about 65% AP. For a high energy binder the flame temperature increases only slightly, with a peak temperature at approximately 30% AP. It is generally observed that the dark zone disappears at about 30% AP[1] which would be consistent with these calculations. The addition of AP to double base binders causes a definite increase in burn rate with smaller particles causing a greater increase than larger particles. The very reactive products from the AP diffuse into the stream of double base decomposition products reacting in a primary diffusion flame analogous to the primary flame in composite propellants. As in composite propellants, adding AP can increase the propellant rate higher than the inherent rate of either the binder or the AP.

Adding HMX to a double base binder results in minimal changes in the burn rate. Data presented in reference 2 shows that adding different sized HMX particles at concentrations up to ~60% did not significantly alter the burn rate. This is not surprising considering that both HMX and double base binder each contain CHON elements and similar energy levels. Calculated flame temperatures varying the percent HMX for double base binders of varying H_{ex} show for high energy binder there is little change in the flame temperature of the propellant. For low energy binder adding HMX increases the flame temperature. The calculated temperatures all increase towards the adiabatic flame temperature of HMX which is higher than any of the double base flame temperatures. Kubota has observed that the dark zone in HMX/double base propellants persists at low pressures and low concentrations of HMX up to about 30% HMX[1,3].

These observations make it apparent that the dominant combustion mechanism is the burning rate of the double base binder, and that the HMX does not contribute significantly

(either in a positive or a negative manner) to the propellant burn rate. Stoichiometrically, HMX is not a true oxidizer and decomposition products from HMX and double base are very similar; neither contains a powerful oxidizing species such as perchloric acid. It appears that the diffusion flame between the HMX and binder is very similar to the individual monopropellant flames, and causes small changes in the burn rate. This is very different from the AP/double base diffusion flame.

From a mechanistic basis one concludes that the AP primary diffusion flame is a dominant combustion mechanism competing with the double base monopropellant flame for control of the burn rate. The effect of the AP diffusion flame is related to both the increased temperature, but is probably more dependent on the increased reactivity of the AP surface products. The fact that HMX has such a small effect in spite of its greater inherent monopropellant rate, one might conclude its monopropellant flame is being interrupted by the double base products. If this were the case, then coarse HMX should cause an increased rate in a double base system (i.e. diffusion distances would be too large to compete with the monopropellant flame, and the HMX would burn at its own rate). The fact that this behavior is not observed leads one to another possibility; that of a large ignition delay time[4]. The actual mechanistic action of HMX in a double base binder is not fully understood at this time.

CONDENSED PHASE CHARACTERISTICS

The initial decomposition reactions begin in the condensed phase. Most ingredients actually melt or go through a molten phase during combustion. Because the thermal wave penetration is relatively shallow, the molten phase is usually only a thin layer on the surface of the propellant (ingredient). Depending on the heat feed back rate from the flame, the condensed phase reactions continue (usually in the molten phase) until the reaction products are gaseous. Some of these reactions will be heterogeneous reactions, where gaseous, intermediate decomposition products react with the thin, molten, liquid phase. Gas phase decomposition products leave the condensed surface at the surface temperature and enter the gas phase as a boundary condition for the processes leading to the flame and the final combustion processes. The contribution of the condensed phase to the combustion process is to provide a concentration of reactive, gaseous intermediates at a given temperature (the surface temperature) to the gas phase which can then react in the gas flame. Depending on the initial pressure or temperature, the composition and temperature of the surface products will vary, and will provide a variation in the rate of reaction in the flame. Thus, although the condensed phase reactions are not the controlling mechanism in the combustion process, they do have a significant influence on burn rate, pressure exponent and temperature sensitivity.

Surface temperature comparisons

Surface temperature is usually measured with fine thermocouples. This is difficult to do especially in crystalline monopropellants such as AP or HMX. However, a large number of investigators have obtained measurements of surface temperature for double base propellants, but only a few have obtained data in a systematic manner varying pertinent variables, such as pressure, initial temperature or propellant composition. The data from those systematic studies[5-10] have been correlated and are plotted in Fig. 3. Other studies where the data are very limited have not been included in the correlations, but it is not likely that they would make a significant change in any of the conclusions. The surface temperature values for double base fall in the general range of 450 to 725 K, and increasing with increasing pressure. Considering the various sources of data a surface activation energy of 5 to 10 Kcal/mole seems to fit the data best.

Although data for pure AP are virtually nonexistent, various sources of surface temperature data for AP in composite propellants were found in the literature and used for a basis of comparison. The extensive data of Powling[11], using an IR detector to measure the surface temperature of AP composite propellants, appeared to be the most consistent, and those data have been included in Fig. 3. More recent data by Zenin[12] have been reported, but not in time to be included in the correlation. For the AP data a surface activation energy of 30 Kcal/mole fits the data best. It is also very apparent that most of the data were obtained at burning rates and surface temperatures well below those of normal interest. The need for experimental surface temperature for rates above 0.1 cm/sec is very apparent. AP has the highest surface temperature of the monopropellants considered with values measured up to 900 K.
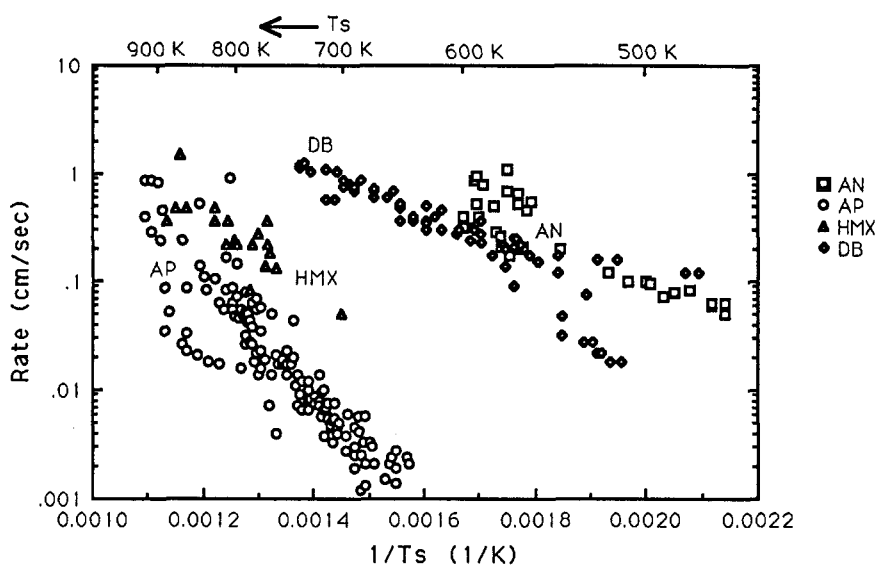
Fig. 3. Comparison of calculated surface temperature and data.

Mitani[13] and Lengelle[14] have reported surface temperatures for HMX (pressed with a small amount of fuel) which have been included in Fig. 3. The HMX data indicate values of 800 to 900 K, essentially parallel to the AP data, and also yield a surface activation energy of ~30 Kcal/mole. Andersen, et al[15] reported hot plate data for pellets of AN, while Whittaker and Barham[16] measured temperature profiles using thermocouples in burning pressed pellets of AN (containing up to 2.5% Cr_2O_3). It is significant that the burn rate catalyst did not appear to have a significant influence on the surface decomposition characteristics. This seems to verify that the gas phase reaction is the controlling mechanism, and the surface decomposition simply accommodates the heat flux from the gas. The AN data indicate a surface activation energy value between ~10 and 15 Kcal/mole. The measured and calculated surface temperatures vary between 500 and 600 K which is in the same range as double base propellants, but significantly lower than AP or HMX.

Condensed phase heat release

Some of the same researchers that measured surface temperatures, also reduced their data to infer the condensed phase heat release, Q_C, particularly for double base propellants[17,18]. The values of Q_C are ~ 50 to 125 cal/gm, exothermic. No data were found for AP or AN, but a limited data set for HMX[14] has been reported. The HMX data also have values from 50 to 125 cal/gm, exothermic. It has been observed that Q_C is proportional to the reaction temperature and decreases with increasing initial temperature[9,18]. This indicates that the surface heat release is proportional to T_s-T_0. It would seem consistent that the amount of energy released would be related to surface temperature rather than pressure. Data have also been reported for composite propellants with values in the range of 30 to 100 cal/gm.

AN is a relatively simple compound due to the fact that it only contains three atoms, HON. This simplicity allows an estimation of the value of Q_C. If it is assumed that free radicals are probably short lived in the condensed phase, then the number of intermediate products involved in the condensed phase reactions is probably limited. To estimate a value of Q_C for AN, thermochemical calculations were made that correspond to five possible nitrogen oxidation states, as nitrogen is reduced from the nitrate ion, through the various nitrogen oxides, to N_2. The results are summarized in Table 1 where a heat of reaction and adiabatic reaction temperature are recorded for each oxidation state.

Table 1. AN Monopropellant Reactions

		ΔH (Kcal)	cal/gm	T (K)
(1) NH_4NO_3	$= HNO_3 + NH_3$	44.5	556	-
(2) NH_4NO_3	$= NO_2 + H_2O + H_2 + 1/2 N_2$	37.6	470	-
(3) NH_4NO_3	$= NO + 2 H_2O + 1/2 N_2$	-6.6	-83	550
(4) NH_4NO_3	$= N_2O + 2 H_2O$	-8.7	-109	625
(5) NH_4NO_3	$= N_2 + 2 H_2O + 1/2 O_2$	-28.2	-352	1247

The initial decomposition of AN to HNO_3 and NH_3, and the subsequent reaction leading to NO_2 are both very endothermic and do not lead to an adiabatic reaction temperature. These are most likely the initial reactions occurring in the condensed phase. The reactions leading to NO and N_2O are both exothermic with calculated reaction temperatures of approximately 600 K, which is the nominally measured surface temperature of burning AN. It is significant to note that the melting temperature of AN is 443 K. Therefore, it would appear that the nitrate is reduced at least to NO in the condensed phase and probable some fraction of the material reacts to N_2O, which is the predominant nitrogen product leaving the surface[19]. Based on these calculations, Q_C values of the order of 80 to 100 cal/gm, exothermic, should be expected for AN.

These basic processes will be similar for different propellant ingredients, whether oxidizer or binder. The actual composition and temperature of the products of the condensed phase will differ for different ingredients and conditions. The associated energy release will also vary for different ingredients.

MONOPROPELLANT FLAME STRUCTURE

Most ingredients used in solid propellants will actually burn as monopropellants (as shown in Figs. 1 and 2). Figure 4 is a schematic of the combustion mechanisms and thermal profile involved in monopropellant combustion. As illustrated, the region of condensed phase reactivity can be relatively thick, especially at low pressures when the thermal wave penetrates deeply into the solid. The thickness of the condensed phase reaction zone is typically the same order of magnitude as the gas phase flame standoff distance. The decomposition products of the condensed phase reactions leave the surface and react in the gas phase to form a premixed, monopropellant flame. Because of the premixed nature of the flame, the thermal profile is very pressure dependent, as illustrated in the figure. The specific temperatures in the figure correspond to AP, but the general concepts apply to any monopropellant. The energy release has been measured for double base propellant, but measurements for AP or HMX are not available. The energy release apparently occurs in a rather thick flame, but very close to the surface. Flame stand-off distances are on the order of 100 μm at low pressures decreasing to 10 μm or less at higher pressures. The actual energy release zone or 'flame' is even smaller. The very small dimensions make experimental measurements of flame zones very difficult.

Double base propellants and, to a lesser extent, HMX both exhibit a two stage flame. For double base propellants the inner flame is ~1200 to 1700 K depending on both pressure and binder energy. A dark zone separates the inner flame from a final flame of ~1500 to 3000 K, again depending on pressure and binder energy. The effect of the heat transfer from the flame
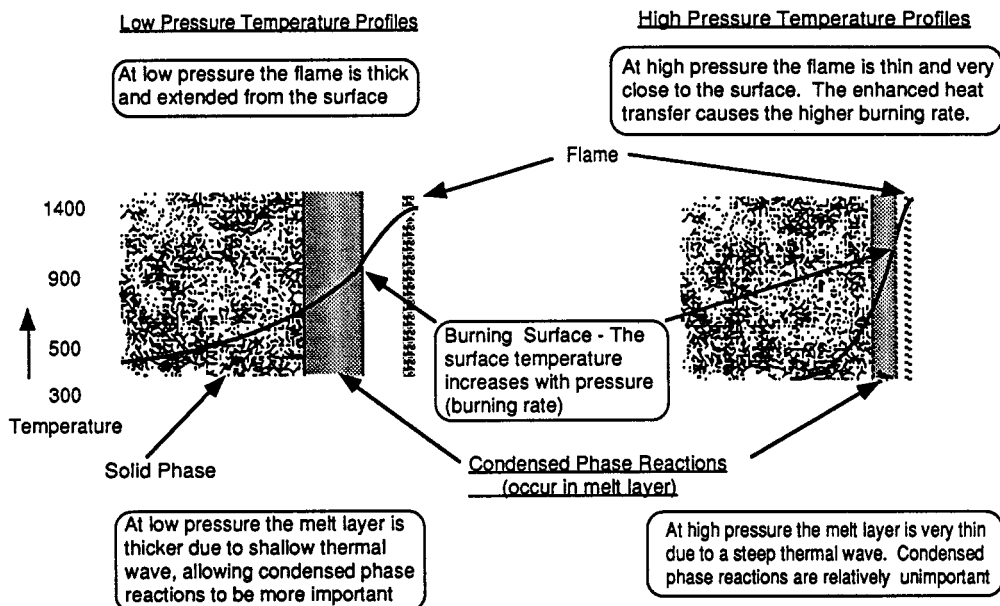

Fig. 4. Monopropellant combustion mechanisms and thermal profile.

on the burning rate of the material is dominated by the inner flame, which in turn, dominates the burning rate. At high pressure (~ 100 atm) the two reaction zones merge, and only one flame is observed at higher pressures. The inner flame is apparently characterized by the reaction of NO_2 to form NO. The NO is relatively stable, leading to the dark zone. The stability of the NO molecule has also been observed in studies of air pollution. The end of the dark zone is characterized by the reaction of NO to form N_2O and ultimately N_2. The HMX flame is much more difficult to study, but shows similar behavior. However, there is no observed dark zone and the inner zone disappears at pressures slightly above atmospheric.

These basic processes will be similar for different propellant ingredients, whether oxidizer or binder. The precise composition and temperature of the products will differ for different ingredients and for different conditions. The corresponding energy release will also vary. However, many of the actual reaction steps in the gas phase will be the same for differing ingredients. For example, the very important gas phase reactions involving NO_2, NO, and N_2O will be the same irrespective of the source. Only the composition and temperature of the reactants will vary for different ingredients. Thus, it should be possible to establish general reaction schemes that should be common for many ingredients. Indeed, Branch[20] at Colorado has shown this to be true for NO_2 flames with varying fuels (i.e. CH_4, C_2H_2).

COMPOSITE PROPELLANT FLAME STRUCTURE

Once the oxidizing and fuel species have diffused together, they can react in a diffusion flame or the oxidizer can still react as a monopropellant., both flames can coexist. Trying to imagine what the flame structure is for composite propellants, varying pressure, oxidizer particle sizes, and everything else that can be involved in a propellant, can be a real problem. Visualizing the flame structure can be compared to the fable of the blind men and the elephant. None of them could see the elephant, and each of them examined a different part of the elephant with their hands. Thus, each blind man had a different perception of what the elephant looked like. Each was wrong in the overall, but each was right for the particular part that they examined.

Speculating on the flame structure of a composite propellant can be analogous. Different researchers have examined different aspects of combustion or of the flame structure, but none of us can actually 'see' what a flame looks like in an actual propellant environment. Figure 5 is a schematic of the solid propellant flame structure that has been proposed in the past[21]. The concepts that are illustrated in Fig. 5 are specific to an AP composite propellant, but can be applied in general to most propellant types and ingredients. The figure illustrates the reaction zones that must be considered in order to understand the very complex combination of combustion mechanisms that occur in propellant combustion. However, all of these characteristics are speculative, like the case of the blind men, and there is a great need for quantitative, definitive work.

Premixed Monopropellant Flame
A dominant mechanism, very pressure sensitive

Interaction between premixed and diffusion flames is the most critical part of any modeling approach

Oxidizer decomposition products can react in either diffusion or premixed flame

Condensed Phase Reactions
Occur in a thin melt layer just below the surface. They are usually of secondary importance

Some oxidizers produce oxidizing rich products which react in a final diffusion flame

Oxidizer

Final Diffusion Flame
Usually of secondary importance, but can be important in interacting with motor acoustics or cross flow or at high pressure

Primary Diffusion Flame
The dominant mechanism in controlling propellant burn rate because of its intense energy release and proximity to the burning surface

Fuel decomposition products react in diffusion flames

Condensed phase mixing of melt layers is usually minimal due to the thinness of the melt layers and the short residence times
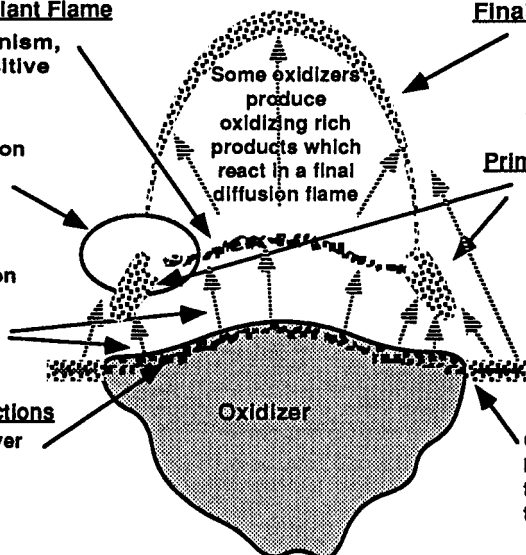
Fig. 5. Solid propellant flame structure and combustion mechanisms.

The interactions between the different flames is critical in understanding the combustion mechanisms, especially the pressure dependence. The diffusion flame is a dominant mechanism (especially for strong oxidizers such as AP), and therefore, understanding diffusion flames is extremely important to understand the various mechanisms in propellant combustion. Even with weak oxidizers such as HMX or AN, the primary diffusion flame is a significant mechanism in the combustion process. In the case of HMX, the energy release in the primary flame can be a very reduced energy level from that of the HMX monopropellant flame. Thus, in the case of HMX composite propellants, the primary diffusion flame can actually 'rob' energy from the combustion process, reducing the effective energy release and the corresponding burning rate.

Diffusion flame effects

Previous diffusion flame analyses used in solid propellant modeling have typically been based on Burke-Schumann type-models, and have assumed an infinite reaction rate in order to achieve an analytic solution to the problem. In actuality, the kinetic rates between the fuel and oxidizer are finite and need to be included as such. Although the geometry of a pure diffusion flame would be independent of pressure, the kinetic aspects of a practical diffusion flame are pressure dependent. Thus, pressure dependent combustion characteristics can be related to the characteristics of the diffusion flame. Also, in considering the interaction of acoustics or cross flow with the propellant flame structure, it is apparent that both will interact primarily with the final diffusion flame. Thus, although the final diffusion flame is usually of a secondary importance in determining the steady state burning rate, it can become a primary factor in determining erosive burning or the unstable combustion response.

Flame interactions

When an oxidixer is incorporated into a propellant environment, the oxidizing species can react either in a monopropellant flame or in a diffusion flame with the fuel species from the binder. The trade-off between how these flames are established for varying conditions and how they interact, is critical to the understanding of propellant combustion. This not only requires an understanding of diffusion flames, including finite kinetics, but also of the interaction of the diffusion flame with the premixed monopropellant flame. The complex flame structure that evolves will also have a complex thermal environment associated with it.

Figure 6 contains a schematic of the temperature profiles that can exist in a typical propellant environment. At the edge of a crystal the surface sees a very hot diffusion flame with a rapidly rising temperature. This is essentially the flame profile that an embedded thermocouple might be exposed to. Slightly in from the edge of the crystal, the thermal profile could go through the monopropellant flame and then a diffusion flame. At the center of a crystal the thermal profile could again go through the monopropellant flame, probably having an
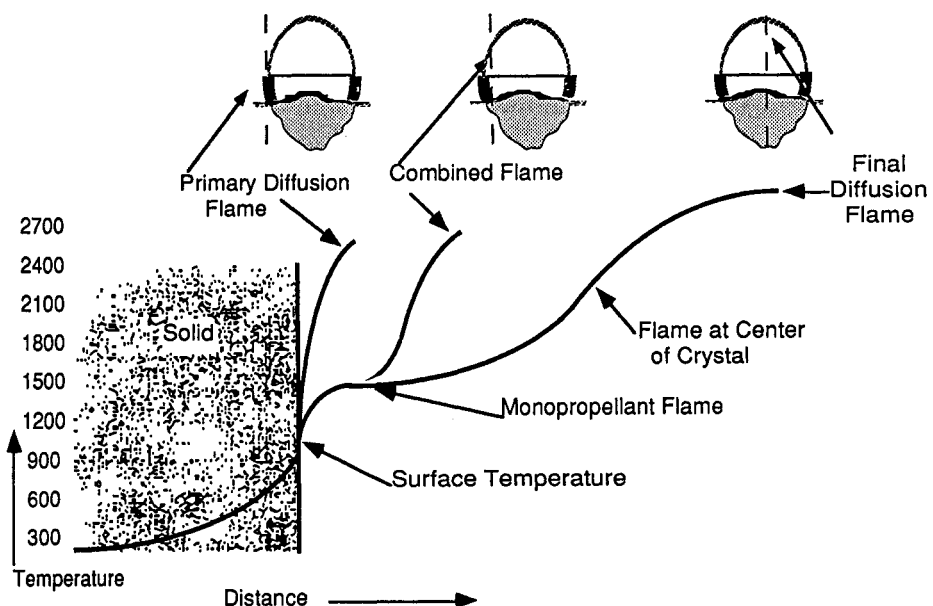

Fig. 6. Thermal profiles that can exist over a single burning crystal of AP.

extended distance of little activity and then a final diffusion flame. The profile would look much like the two stage flame of double base propellants. A thermocouple would not be able to measure a profile like this unless it could be embedded in the crystal. Data from thermocouples have been, and continue to be, an important source of information concerning the flame structure of burning propellants. However, care must be taken to recognize the limits of thermocouple measurements, especially the fact that they can only be placed in the binder, and their measurements will always reflect the thermal profile at the edge of a crystal, bur not the profile at the center of a crystal.

The primary diffusion flame can have a higher temperature than the monopropellant flame, as illustrated for AP, or it can have a lower temperature, as would occur with HMX. In either case, the temperature profiles are very complex and will vary across the surface of an oxidizer crystal. The flame standoff distances of the flames relative to each other will also vary with particle size and with pressure, thus having a significant effect on the burning rate and the pressure exponent. To model these phenomena accurately will require a three dimensional analysis using very fine numerical grids and probably adaptive griding techniques.

Pressure effects on flame structure

Because of the complexity of the flame structure, interpreting the effects of pressure on the interaction of the monopropellant and diffusion flames is a very difficult, but important task if one is to understand how the flame structure changes with pressure. Figure 7 illustrates how the complexity of the flame structure may change for varying pressure.

Low Pressure Flame Structure

Low pressure flames consist of primary flame only.

Monopropellant flame cannot be established due to pressure sensitivity of kinetics. Monopropellant flame height is preemted by primary flame.

Diffusion flame is lifted from surface due to slower kinetics

Melt layer is thick due to shallow thermal wave. Condensed phase reactions can become more important

Moderate Pressure Flame Structure

Moderate pressure flames consist of typical BDP structure (3 flames).

Monopropellant flame moves closer to the surface and competes with the primary diffusion flame

Diffusion flame is slightly pressure dependent and shape does not vary except for competition with monopropellant flame

Melt layer is thinner due to steeper thermal wave. Condensed phase reactions become less important

High Pressure Flame Structure

High pressure flames consist of two flames.

Monopropellant flame moves very close to the surface and dominates combustion process

Primary flame cannot compete with monopropellant flame. Final diffusion flame can become important

Melt layer is very thin due to steep thermal wave. Condensed phase reactions become less important relative to dominant mechanisms
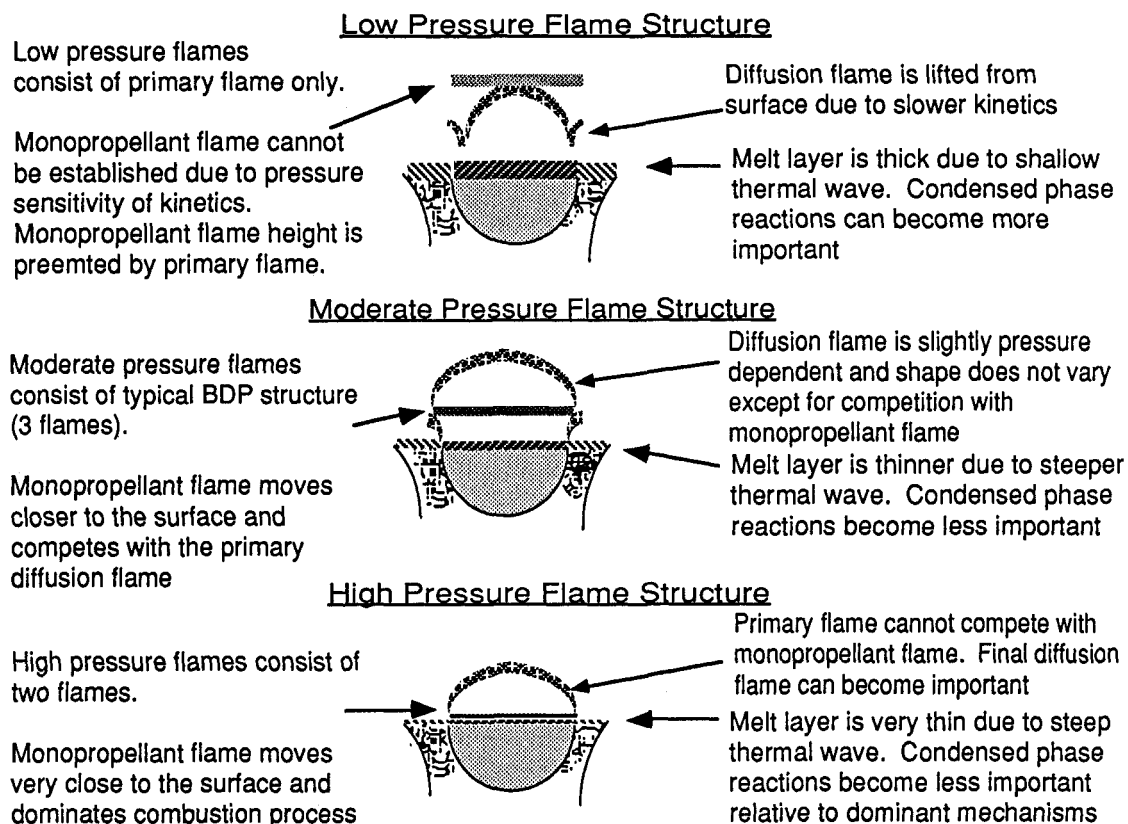
Fig. 7. Pressure effects on propellant flame structure.

At low pressure the monopropellant flame can have a standoff distance greater than the diffusion flame, thus precluding the formation of a monopropellant flame. However, at increasing pressure, the monopropellant flame can move closer to the propellant surface, minimizing the diffusion flame effects. This is due to the strong pressure dependence of the premixed flame versus the weak pressure dependence of the diffusion flame (due to the kinetic

1. At ignition, the initial flame structure is a primary flame only. The monopropellant flame is preempted because of very small diffusion distances

Diffusion flame forms (no monopropellant flame)
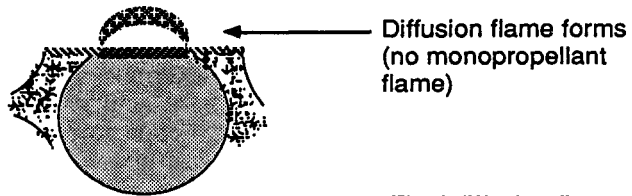
2. As the particle burns, the monopropellant flame is established and a classical BDP flame structure develops

Final diffusion flame

Monopropellant flame

Primary diffusion flame
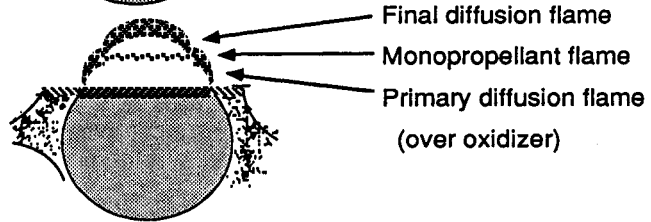
(over oxidizer)

3. Eventually the primary flame becomes very oxidizer rich, and flips over the binder giving a mushroom type of structure

Final diffusion flame

Monopropellant flame
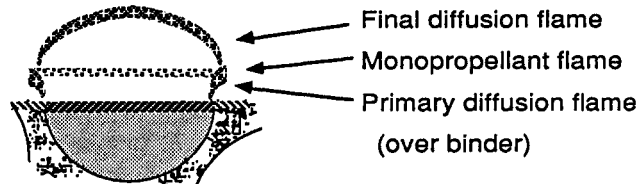
Primary diffusion flame

(over binder)

Fig. 8. Changes in propellant flame structure during the geometrical cycle of a burning particle.

aspects of the flame). The changes with pressure obviously effect the characteristics of the pressure exponent, but also have a direct impact on the propellant's response to pressure perturbations (i.e. its response to combustion instability). A similar change in flame structure can result from changes in particle size, small particles having a structure similar to the low pressure structure, while larger particles will have a flame structure more similar to high pressure.

Geometry effects on flame structure

As a particle burns the amount of fuel binder that is available to burn in the diffusion flame changes. Therefore, interpreting the effects of these geometrical changes on the interaction of the monopropellant and diffusion flames is also a very difficult, but important task if one is to understand the propellant combustion mechanisms. Figure 8 illustrates the geometrical change in flame structure that can occur as a particle burns. When the particle is first exposed to the combustion atmosphere, it is in a very fuel rich environment due to the fact that the particle is surrounded by fuel and only a small amount of oxidizer is initially exposed to the combustion front. Because of the fuel rich environment the initial flame that is established as the particle ignites, it most likely a diffusion flame. There is probably too much fuel available for the monopropellant flame to be established.

As burning progresses and more of the oxidizer is exposed, there is less fuel available and the monopropellant can become established consuming part of the oxidizer decomposition products. This allows the classical flame structure to develop as shown in part 2 of the figure. Ultimately, the primary flame will become very oxidizer rich due to the very thin layer of fuel that surrounds the oxidizer. In this case the flame will bend over the fuel, causing the mushroom shaped structure shown in part 3 of the figure. These changes in flame structure will also depend strongly on particle size, small particles having a structure similar to the structure in part 1 of the figure, while the flame structure shown in part 3 will persist for most of the life time of larger particles. As burning continues the process will reverse as the availability of fuel changes going through a flame structure similar to part 2 and part 1 of the figure. As the particle burns out it will most likely revert to the diffusion flame structure of part 1.

IMPROVING THE STATE OF UNDERSTANDING

Progress is being made in studying the flame structure involved in propellant combustion. Indeed, many papers at this symposium are directed to that subject. Advanced diagnostic techniques are being developed that allow a more quantitative measure of temperatures and species during different phases of the combustion process. Significant progress has been made in studying the fundamentals of the condensed phase chemistry of propellants and of

monopropellant combustion. Mass spectrography has been applied to AP, HMX, RDX and double base to determine the reaction products leaving the surface and in the reaction zones (e.g. Refs. 22-25). More advanced laser diagnostics are also being used to identify individual species both in the condensed phase and within the flame. Progress is being made in the area of modeling. Detailed models based on the conservation equations and including extended kinetic mechanisms have been published on AP, HMX, RDX and NG (e.g. Refs. 25-31). Several other researchers are publishing similar models for different homogeneous materials. These works are leading to further understanding about monopropellant combustion.

Similar progress is more difficult to achieve with understanding diffusion flames, especially within the context of propellant combustion. Experimental work is usually done with burners, and unfortunately they are much larger than the dimensions associated with propellants. Probing the very microscopic flame zones associated with diffusion flames of the dimension seen in solid propellants is a very formidable task. In this instance we are very much like the blind men referred to above. Because of these inherent difficulties, a cooperative effort between experimentalists and theoreticians will be required to unravel a realistic, quantitative picture of our elephant, the flame structure of composite propellant.

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