JOURNAL OF PROPULSION AND POWER
Vol. 13, No. 4, July–August 1997

Mechanism of Burning Rate Enhancement of Composite Solid Propellants by Ferric Oxide

Satyanarayanan R. Chakravarthy,* Edward W. Price,† and Robert K. Sigman‡
Georgia Institute of Technology, Atlanta, Georgia 30332-0150

This paper reports a series of experimental studies performed on sandwich propellants, wherein a matrix lamina of particulate oxidizer and polymeric binder is sandwiched between two ammonium perchlorate (AP) laminae. The catalyst (ferric oxide) is incorporated in the matrix lamina. The variables are pressure (0.345–6.9 MPa), matrix lamina thickness, catalyst concentration, matrix mixture ratio, types of oxidizer and binder, and the dispersion ability of the catalyst. The combined results indicate that, under the conditions tested, near-surface reactions associated with the particulate AP/binder contact lines on the burning surface assume significance in the presence of the catalyst. These reactions are further augmented by the presence of the leading-edge portion of the diffusion flame above the interface of the matrix and AP laminae.

I. Introduction

THE burning rates of ammonium perchlorate (AP) composite solid rocket propellants are routinely adjusted by the addition of small amounts of ballistic modifiers to the propellant formulation. For increasing the burning rate, the most common catalyst is iron oxide (IO, Fe_2O_3). The rate-controlling steps in the combustion of composite propellants have been debated for 40 years, and the mode of action of ballistic modifiers remains uncertain because of the remaining debate about the rate controlling steps.

Kishore and Sunitha[1] have made a nearly comprehensive survey of the literature on burning rate catalysis spanning roughly two decades up to the late 1970s. They observe that a wide variety of sites and mechanisms of action of the catalysts are proposed by the numerous studies. Subsequent studies, steadily decreasing in number, have done little to alleviate this situation.

The diverse and fragmentary nature of the literature pertaining to the problem makes it difficult to summarize the different viewpoints presented therein. Reported studies include effects of catalysts on the combustion and thermal decomposition of AP, condensed mixtures, model propellants, and regular propellants. Although this study is concerned mainly with the effect of iron oxide (IO), it seems natural to consider it as part of a broader class of transition metal oxides from a chemical point of view, and, hence, studies with other such additives cannot be ignored.

Proposed mechanisms include 1) physical effect of IO accumulated on the surface getting heated up from the flame and aiding binder regression by direct contact[2]; 2) effect on binder melt flow behavior, physically or chemically[3]; 3) catalysis of binder thermal degradation at the urethane linkages in the condensed phase at low pressures (2–7 MPa)[4,5]; 4) enhanced near-surface breakdown of heavy fuel molecules,[6–10] better with finer AP particles,[9] supplying more reactive fuel species to the O/F flame,[6,7] thereby bringing it closer to the surface and increasing the burning rate[6,7,11]; 5) action in the gas phase by a) modification of gas phase reactions by chloride derivatives of the catalyst,[9] b) exothermic breakdown of the catalyst by reactions with other species,[11] c) catalysis of the O/F flame,[12,13] and/ or d) catalysis of $HClO_4$ decomposition[14] (heterogeneous surface reactions not excluded[10]); 6) heterogeneous gas phase exothermic reactions between catalyst particles and $HClO_4$ (Ref. 15); 7) gas phase and/or heterogeneous reactions in crevices between fuel and AP[12]; 8) catalysis of some process in the vicinity of the AP/binder interface[16]; 9) catalysis of AP deflagration,[12,17] or decomposition[13] (by proton transfer[10] or electron transfer[18]); 10) action in the condensed phase: a) at the AP/binder interfacial surfaces,[8,9,19] b) by altering the decomposition products of AP and binder,[10,11] or c) by catalyzing $HClO_4$ decomposition, the products of which eventually enhance binder degradation,[20] or by catalyzing the oxidative polymer degradation by $HClO_4$ (Ref. 21); and 11) formation of thermally unstable metal perchlorates[10,18] or metal perchlorate amines.[22]

In spite of the diverse views on the problem, some general impressions are gained and are noteworthy. It appears that copper chromite (CC) and IO are most effective among the class of transition metal oxide additives.[1,6,7] CC acts better on AP,[17] whereas IO acts better when both AP and binder are involved.[12,16,21] CC is a better catalyst at high pressure, and IO at low pressure.[19]

Many investigators have proposed multiple mechanisms. In some cases, the results do not allow resolution among these mechanisms, and in some others, the investigators believe that a single mechanism cannot exclusively account for the net catalytic effect.[1] Many of these investigations have been carried out under various conditions that are not directly related to rocket operating conditions, and as such, their inferences are restricted in applicability to specific domains of propellant burning. It would be desirable to delineate domains of test conditions (pressure, particle size, etc.), in which the different mechanisms predominate over the others in controlling the burning rate of the propellant.

The present study is part of a larger investigation on the combustion mechanisms of solid propellants using the sandwich-burning method. This method provides relative ease of preparation and variation of test samples, and observation and characterization of the combustion behavior. This method also provides a rich background of previous studies for comparison with new results. Earlier results are available for sandwiches of AP-binder–AP laminae, in which the binder lamina consisted of 1) pure binder,[23] 2) catalyzed binder,[6,7,24] and 3) particulate AP-filled binder.[25,26] The present study concerns combustion with various iron catalysts and oxidizers (primarily Fe_2O_3 and AP) in the binder lamina.

Received Feb. 20, 1996; revision received Feb. 19, 1997; accepted for publication April 8, 1997.

*Post Doctoral Fellow, School of Aerospace Engineering.

†Regents' Professor Emeritus, School of Aerospace Engineering. Fellow AIAA.

‡Senior Research Engineer, School of Aerospace Engineering.

Considering the complex nature of the problem, the goal of this study would be accomplished if evidence were obtained that indicated the possible sites of predominant action of the Fe_2O_3 for the given initial geometry of ingredients. Attempts at resolving the exact chemistry are beyond the scope of this work, although plausible mechanisms may be proposed.

II. Background

Sandwiches with AP-filled binder laminae can be thought of as a two-dimensionalized simulation of the microscopic region included by adjacent coarse AP particles in a typical propellant with bimodal AP size distribution.

In the case of pure binder sandwiches, the leading edges of the oxidizer/fuel (O/F) diffusion flames (LEFs) are the sites of major near-surface heat release[12,16,27,28] and, hence, behave as rate controlling.[13,23,29] For thin nonmelting binder lamina, e.g., polybutadiene acrylonitrile acrylic acid (PBAN), the LEFs are multidimensionally coupled (in terms of heat feedback to the surface), and this is reflected in a maximum in the burning rate at a binder lamina thickness ~50–75 μm (Fig. 1). When ferric oxide is present in the binder lamina,[6,7,24] it accumulates on the binder surface, facilitating breakdown of heavy fuel molecules into lighter, more reactive species. This enables the LEFs to be located closer to the surface, resulting in an increase in the burning rate.

The mechanics of AP-filled sandwiches have been elucidated in detail recently.[25–27] It is briefly revisited here to establish some terminology used in this study, and also to serve as a comparison with the situation when the catalyst is present. With AP-filled binder laminae, the previous LEFs are designated as lamina leading-edge flames (LLEFs), to distinguish them from smaller LEFs that could exist above the fine AP particles, particle leading-edge flames (PLEFs), in the AP/binder matrix lamina. The mutual interaction of the LLEFs again results in a peak in the burning rate vs lamina thickness curve, but at a matrix lamina thickness ~225–275 μm (Fig. 1). The larger thickness is because of the diluting effect of the AP particles; but they do not act as just a diluent:

1) The matrix is less fuel rich than the pure binder, and, hence, the stoichiometric surface above the lamina interface shifts inward.

2) The lateral extent of the fuel side of the LLEFs is increased.

3) The total heat release in the LLEFs is increased, enabling the flame to stand closer to the surface.

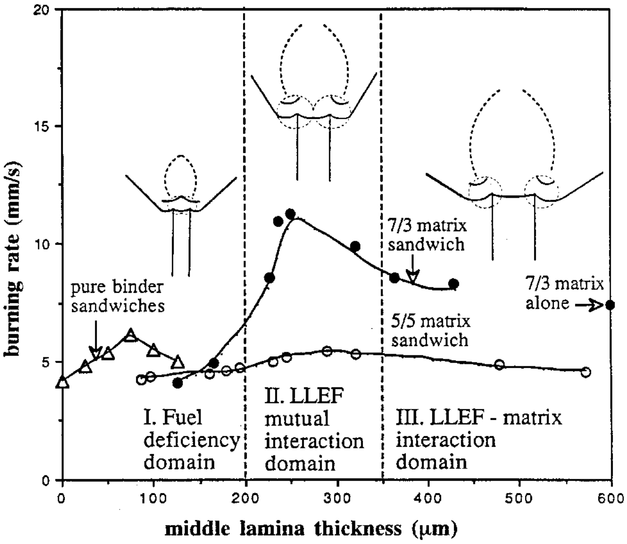

Fig. 1 Typical dependence of uncatalyzed sandwich burning behavior on matrix lamina thickness for pure PBAN binder, and AP/PBAN matrix.

These effects are favorable for direct heating of the matrix lamina, and so condensed phase lateral heat transfer from the AP lamina across the lamina interface plane is reduced. This is reflected in 1) reduced width of the smooth band[23] on the AP surface adjoining the lamina interface and 2) reduced extent of AP retardation in that region. When the matrix mixture is adequately less fuel rich, so that the premixing matrix gases can sustain combustion (as in AP/PBAN = 7/3), and when the thermal wave thickness >> fine AP particle size (small particles, low pressure), a premixed canopy flame exists above the matrix lamina, connecting the fuel-rich sides of the LLEFs; when the thermal wave thickness ~ fine AP particle size (large particles, high pressure), LEFs are attached to the individual fine particles, resulting in PLEFs.

The matrix flame does not control the rate, but augments the mutual interaction of the LLEFs (Fig. 1).[27] For large matrix thickness, the LLEFs are uncoupled, but the rate is still slightly higher than that of the matrix alone. This indicates a domain of LLEF-matrix interaction, where the interaction between a single LLEF and processes associated with the matrix (either in the gas phase, condensed phase, or heterogeneous) are rate controlling. It will be seen in this paper that this domain assumes importance in the presence of the catalyst.

III. Experimental

A. Experimental Techniques

Three principal techniques were employed in this study: 1) combustion videography, 2) examination of quenched samples in the scanning electron microscope (SEM), and 3) hot-stage (optical) microscopy (HSM) of ingredients. These techniques are rather routine and are detailed elsewhere.[24,25] Besides serving as a tool for macroscopic flame structure and surface profile studies, the video pictures were also used for burning rate measurements. Flame front positions in successive frames (typically 10–40 points, more for lower rates) were fitted with a straight line in the least-square sense, with a correlation ≥99.9%. The slope of this line gave the burning rate. Approximately 50% of the data points, selected at random, were checked by repeated tests for reproducibility within 5% variation. In the combustion experiments, the samples were coated with a very thin layer of high vacuum grease to inhibit burning down the sides, and were burned in a nitrogen atmosphere. The heating rate in the hot-stage experiments was ~3°C/s, and they were performed at atmospheric pressure in an argon atmosphere.

B. Samples

Fabrication of sandwiches is also detailed elsewhere.[25] The catalyst was thoroughly mixed in the binder first, before adding the oxidizer particles. All of the ingredients for the matrix were weighed within an error of 0.5%. The position of the samples in the oven was inverted periodically during the curing period to prevent the oxidizer particles in the matrix from settling on to one side of the sandwich as a result of gravity. Different size levels of AP particles were used, with appropriate designations: the 2-μm AP was a mixture of AP particles of that size and hydroxyl-terminated polybutadiene (HTPB) prepolymer; the 10-μm AP is from the same batch as used in previous studies[26]; the 33-μm AP and 75-μm AP are those that remained between sieves of mesh sizes 37 and 30 μm, and 90 and 75 μm, respectively. The particle sizes of ammonium dinitramide (ADN), hexanitro hexaazaisowurtzitane (HNIW), and cyclotetramethylene tetranitramine (HMX) were nominally 40, 10, and 10 μm, respectively. The potassium perchlorate (KP) nominal size was about 30 μm. No attempt was made to quantitatively characterize the size distributions of these oxidizer particles beyond ascertaining on the optical and/or SEM that samples of these ingredients did not contain particles of significantly different sizes than just specified. It is considered that such a qualitative approach is sufficient for the purposes of this study. The form of availability of the 2-μm AP restricted it to be used with HTPB-based binders only, and

Table 1 Binder compositions

				Curing agent	
No.	Binder	Prepolymer, %	Plasticizer, % (DOA)	Type	Amount, %
1	PBAN	64.14	15.00	ECA	20.86
2	HTPB-DDI	69.07	16.77	DDI	14.16
3	HTPB-IPDI	75.73	18.39	IPDI	5.88

up to a common maximum ratio of AP/binder = 65/35 with the different curing agents. Three different binder types were employed, and their compositions are given in Table 1. Throughout the text, the designations HTPB-IPDI and HTPB-DDI are used to denote HTPB cured by isophorone diisocyanate (IPDI) and dimeryl diisocyanate (DDI), respectively. 1-2 μl of a cure catalyst, dibutyl tin dilaurate (T-12) was usually added to 5 g of a HTPB-based matrix mixture. This enabled curing of HTPB samples in a day, instead of a week. [T-12 acts on diisocyanate curing agents and could not be used with PBAN/ECA (epoxy curing agent) binder.] The addition of T-12 does not seem to significantly alter the physical behavior of HTPB binder, as observed on the hot stage. The Fe_2O_3 used in this study, unless stated otherwise, is called Pyrocat (manufacturer's specifications: Nanocat™ SFIO catalyst, lot 3-1-125, α-type, particle size 0.003 μm, specific surface area 270 m^2/g, density 0.05 g/cc).

IV. Results

This section is a listing of results with detailed specifications of the test conditions. The implications of the results are discussed in Sec. V.

A. Effects of Matrix Lamina Thickness, Catalyst Concentration, and Matrix Mixture Ratio

Figure 2 shows the dependence of the sandwich burning rate on matrix lamina thickness for 0.2 and 1% Pyrocat in a matrix of AP/PBAN = 7/3 (Fig. 2a) and AP/PBAN = 5/5 (Fig. 2b) at 2.1, 3.5, and 6.9 MPa. The 10-μm AP was used in these tests. The burning rate vs matrix thickness trend for the corresponding uncatalyzed sandwiches (taken from Ref. 25) are presented for comparison. In general, the scatter in the data is slightly-to-considerably more when the catalyst is present; more at the 1% level than at the 0.2% level, and more for a mixture ratio of 5/5 than for 7/3. The AP/PBAN = 5/5, 1% Pyrocat sandwich data are highly scattered, but do not indicate any conspicuous dependence of the burning rate on the matrix lamina thickness. The scatter is not unexpected because the 5/5 mixture is in the region of flammability limits; the uncatalyzed 5/5 matrix alone does not sustain combustion, whereas the catalyzed ones barely burn, at very low rates. However, the following broad features are noted:

1) The 0.2 and 1% catalyzed AP-filled sandwich burning rates are several times higher ($\geq$100%) than corresponding uncatalyzed sandwich rates, compared to a relatively marginal ($\sim$30%) increase in the burning rate of pure PBAN binder sandwiches with 10% catalyst.[24] (The corresponding curves are not shown for comparison in Fig. 2 in the interest of clarity.)

2) The 5/5 matrix alone begins to sustain combustion in the presence of as low a catalyst level as 0.2%, and the 7/3 matrix displays a major increase in the burning rate when catalyzed.

3) The catalyzed 5/5 matrix rates are very low, and the samples burn in a smoldering fashion, without a conspicuous visible flame; the pressure dependence of their burning rates is very weak.

4) The burning rates of the catalyzed 5/5 sandwiches are several times higher than their corresponding matrix rates. On the other hand, the 7/3 sandwiches burn only slightly faster than their corresponding matrices.

5) It must be remembered that no matter how high the catalyzed sandwich rates are, they should logically tend to the AP rate shown on the left ordinate line in Figs. 2a and 2b, in the limit of zero matrix lamina thickness. (This cannot be effectively tested because AP-filled sandwiches with very thin matrix laminae cannot be fabricated practically.) The curves show that even a thin lamina of matrix is sufficient for major catalytic action; it is greater for higher AP loading and catalyst concentration in the matrix.

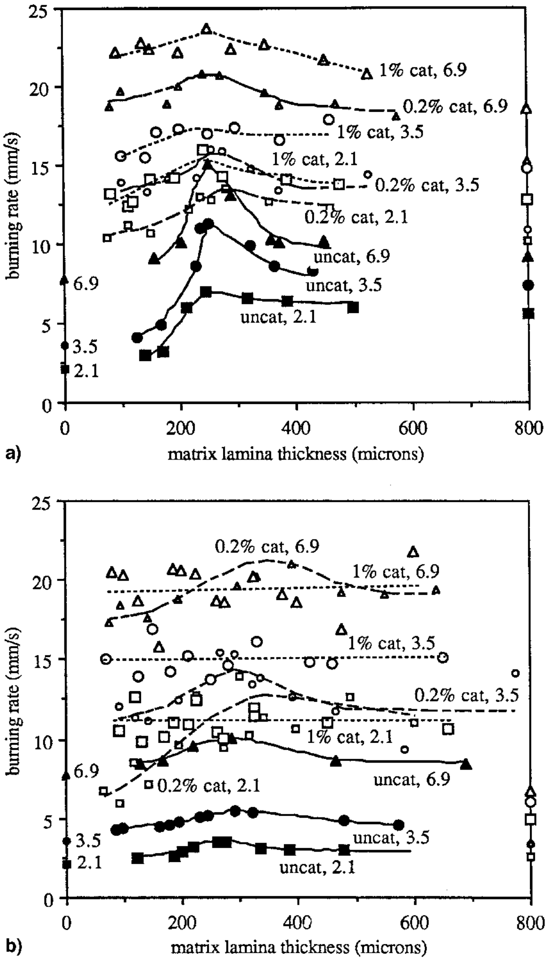

Fig. 2 Dependence of burning rate on matrix lamina thickness for uncatalyzed and catalyzed AP-filled sandwiches at different pressure levels (noted in MPa). Burning rates of pressed AP are shown on the left ordinate, and those of matrix burning alone on the right ordinate lines. AP/PBAN = a) 7/3 matrix and b) 5/5 matrix.

6) The effect of catalyst concentration (0.2 vs 1%) is slight in the case of the 7/3 samples and the 5/5 matrix; it is nearly negligible for the 5/5 sandwiches, except perhaps in the thin matrix lamina limit. Weak dependence of catalytic effect on the catalyst concentration is also reported in the literature.[4,9,15]

7) Except for the case of the 5/5, 0.2% catalyst sandwiches in the thin matrix lamina limit again, and the dependence of sandwich burning rates on the matrix lamina thickness is weakened in the presence of the catalyst.

B. Surface Profile and Features

Sandwiches of the type in item Sec. IV.A in the previous text were quenched by rapid depressurization while burning, and their quenched surfaces were examined in the SEM. The matrix and the lamina AP in the immediate vicinity of the lamina interface burn down so fast, compared to the outer region of the AP laminae, that the surface profile assumes an almost V shape. This makes SEM observations difficult. No remarkable differences are seen between the various quenched samples in an overall sense. A typical quenched surface is

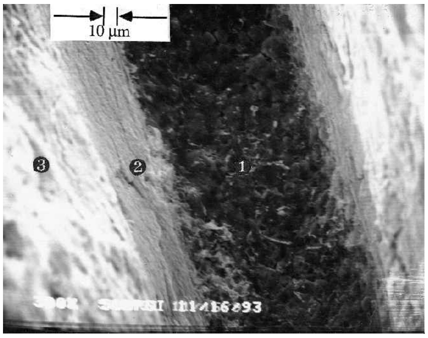

Fig. 3 Quenched surface of a typical catalyzed AP-filled sandwich: ❶ matrix surface, ❷ dry band in the AP lamina, ❸ frothy surface of the AP lamina (not in focus).

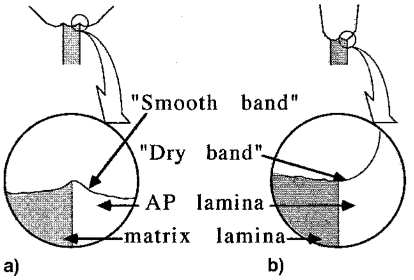

Fig. 4 Typical burning surface profile for AP-filled PBAN sandwiches: a) uncatalyzed and b) catalyzed by Pyrocat.

presented in Fig. 3. Figure 4 shows a typical sketch of the surface profile of these sandwiches in comparison to that of the uncatalyzed case. The following features are noted:

1) There is no retardation in the regression of the AP lamina in the immediate vicinity of the lamina interface in the case of catalyzed sandwiches, as against such a protrusion in uncatalyzed sandwiches.[26] The AP lamina surface in that region has a curvature that is concave upward.

2) The AP surface in the immediate vicinity of the interface has a dry and parched appearance (dry band), as against a smooth and soft surface region (smooth band) in the uncatalyzed sandwiches. The dry bandwidth is much smaller than the corresponding smooth bandwidth.

3) Accumulation of catalyst particles can be observed as sporadic thin white filigrees (size >> catalyst particle size), randomly distributed on the surface of the matrix lamina. The extent of accumulation is lower at the 0.2% catalyst level when compared to the 1% level. Considering the high oxidizer loading, low catalyst content, very fine size of the catalyst, and the fact that the catalyst is in the binder, accumulation of the catalyst cannot be expected to be as high as in earlier work, with sandwiches having 10% IO in pure binder lamina.[6,7,24] Catalyst accumulation in propellants is also reported in the literature.[2,6]

C. Combustion Videography of Very Thick Sandwiches

Video pictures of burning of sandwiches with 10-μm AP/PBAN = 7/3 and 5/5, 1% Pyrocat matrices of lamina thickness > 1000 μm (much larger than typical values) were taken. Figure 5 shows frames from such video pictures for the two mixture ratios. The pictures show some protrusion of the matrix lamina for the 5/5 matrix (Fig. 5a), whereas no such protrusion is found in the case of the 7/3 matrix (Fig. 5b). The burning rates of these sandwiches agree very well with the burning rates of sandwiches in the thick limit of matrix lamina shown in Fig. 2.

D. Effect of Oxidizer Type

Five different oxidizers, AP, KP, ADN, HNIW, and HMX, were tested in conjunction with PBAN (oxidizer/PBAN = 7/3), with and without 1% Pyrocat. Attempts to study ammonium nitrate (AN) did not succeed because of the lack of proper wetting properties between that oxidizer and PBAN. In all cases, the oxidizer/PBAN matrix was sandwiched between two AP laminae.

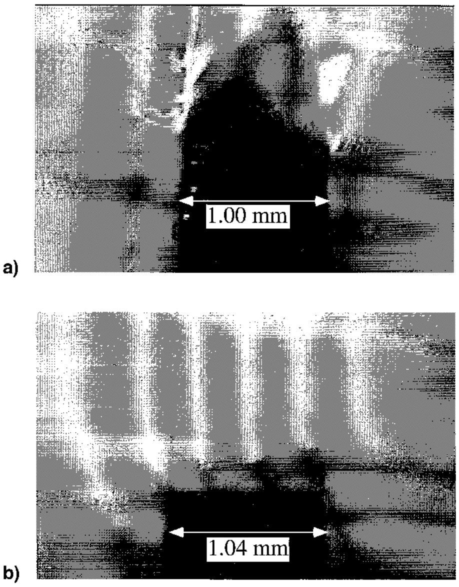

Fig. 5 Video pictures of the combustion of sandwiches with a very thick lamina of 10-μm AP/PBAN, 1% Pyrocat matrix at 3.5 MPa. AP/PBAN = a) 5/5 and b) 7/3.

The rationale behind sandwiching these matrices by AP laminae is to see how the matrix burning responds to the presence of a pair of LLEFs. Ideally, it would be desirable to test sandwiches with the same oxidizer in the matrix and oxidizer laminae, but this could not be done because 1) some of the materials (notably ADN and HNIW) were available only in very small quantities, and 2) safety concerns about pressing pellets of these materials persist. However, the matrix lamina thickness in all of these sandwiches was designed to be ~375–400 μm, to be out in the LLEF–matrix interaction domain rather than the LLEF mutual interaction domain (see Fig. 1).

It was difficult to obtain these different oxidizer particles in the same size range. Also, the particle size effects of these oxidizers are either unknown or mostly different from each other. In any case, the available supplies seem to fall into two size ranges: 10–20 μm for HMX and HNIW, and 30–40 μm for KP and ADN. For effective comparison, the 10-μm AP was used in connection with the first range, and the 33-μm AP was used for the second range.

The ratios of the burning rates of catalyzed and uncatalyzed samples (both sandwiches and matrices) are shown in Fig. 6. This parameter helps reduce the number of curves by half, but inevitably conceals the actual burning rate information. However, it would suffice for the present purpose to note that the burning rates of all samples at a given pressure are comparable on an order of magnitude basis (1.5–8 mm/s at 0.69 MPa; 9–25 mm/s at 6.9 MPa), except HMX matrices, which are lower by one order at every pressure level (0.6 mm/s at 0.69 MPa; 2 mm/s at 6.9 MPa). It is seen clearly from Fig. 6 that the burning rate increase is markedly the highest for AP (≥100%), with the curves corresponding to the other oxidizers lying around a burning rate ratio of unity or slightly more (marginal catalytic effect). Tests on propellants with different oxidizers found in the literature also support the choice of AP for maximum catalysis.[14,15]

E. Effect of Susceptibility of the Binder to Melt Flow

The susceptibility of HTPB binders to melt before vaporization is significantly altered by the choice of different diisocyanate curing agents, which in turn is different from that of PBAN cured by ECA. Aspects related to binder melt flow,

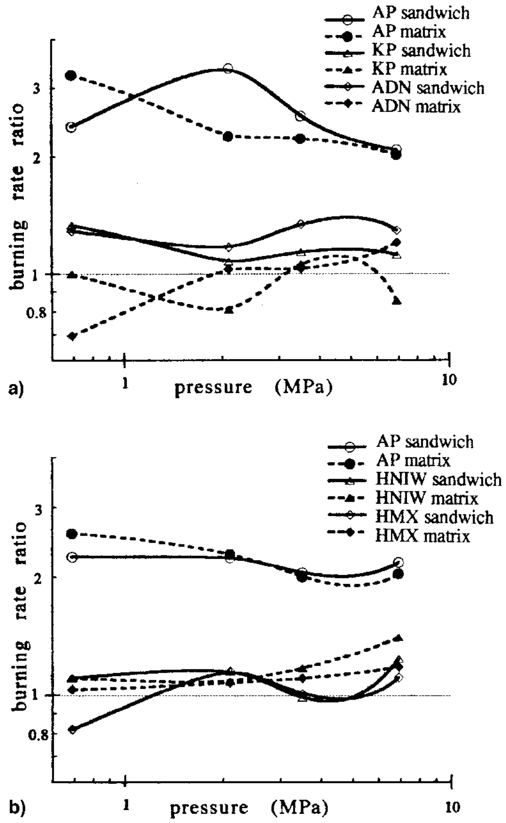

Fig. 6 Ratio of burning rate of catalyzed to uncatalyzed samples with oxidizer-filled PBAN matrices (oxidizer/PBAN = 7/3) in two oxidizer particle size categories: a) 30–40 and b) 10–15 μm.

such as plateau burning behavior of propellants, are addressed in detail in a separate paper.[30] It would suffice here to point out that, as observed in the hot-stage microscope, PBAN melts above 450°C, HTPB–IPDI melts slowly between 300–360°C, whereas HTPB–DDI melts rather abruptly at 230°C. All of these binders vaporize vigorously at 500°C, a value not too different from the decomposition temperature of AP. The hot-stage microscope experiments,[31] and various other combustion tests with pure binder as well as AP-filled sandwiches, have indicated that a qualitative order of increasing susceptibility for melt flow of the binders considered in this work is PBAN < HTPB–IPDI < HTPB–DDI. It should be recorded here that the addition of Pyrocat to the HTPB samples seems to retard the curing process, and advances the onset of melting (conpicuously noticeable in HTPB–DDI) to a lower temperature. The implications of this has been reported in the literature.[4,5,32]

Tests on sandwiches and matrices with and without 1% Pyrocat in a mixture of these binders and the 10-μm AP in the ratio AP/binder = 7/3 resulted in Fig. 7. The sandwiches have a matrix lamina thickness of ~250–275 μm, corresponding to maximum burning rates in Fig. 2. Figure 7a shows burning rates vs pressure for the uncatalyzed samples. In the case of PBAN, the sandwich and matrix curves are more or less parallel to each other. The HTPB–IPDI matrix curve exhibits a plateau in the pressure range 0.7–2 MPa, an effect suspected to be caused by the binder melt flow. The corresponding sandwich burning rate increases steadily with pressure in the entire pressure range tested. The HTPB–DDI matrix does not sustain combustion in the entire pressure range tested; however, it tends to burn, but self-quenches soon after ignition in the low-pressure range 0.35–0.7 MPa. The corresponding sandwich burning rate increases in that pressure range, but subsequently falls back to the AP rate at higher pressures. Above 2.1 MPa, when the AP begins to self-deflagrate, the AP laminae lead the sandwich burning surface (as can also be seen in the video pictures).

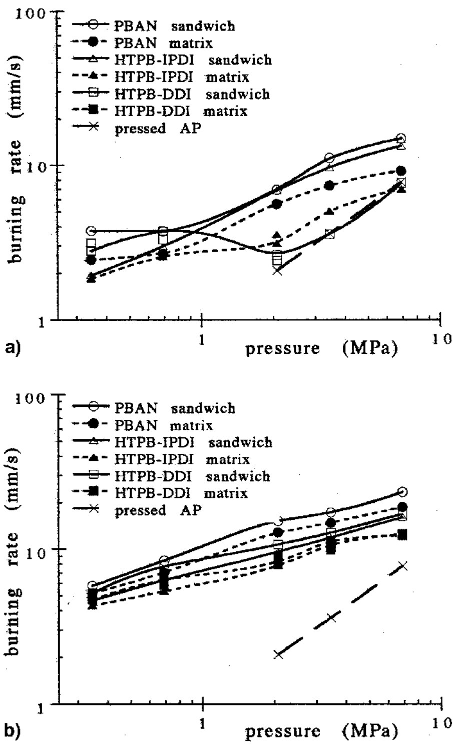

Fig. 7 Effect of binder melt flow characteristics on the burning rate of sandwiches and matrices of 10-μm AP/binder = 7/3: a) uncatalyzed and b) catalyzed by 1% Pyrocat.

Figure 7b shows the burning-rate curves for the catalyzed samples. The overall rates for all of the binders are substantially higher than for their corresponding uncatalyzed samples. Also, in all of the cases, the corresponding matrix and sandwich curves are almost parallel to each other. In fact, the differences in the curves for HTPB–IPDI and HTPB–DDI are slight. The PBAN rates are slightly higher than those of the HTPB-based samples. The effects caused by binder melt flow witnessed in the uncatalyzed situation are considerably washed out when the catalyst is present.

F. Effect of AP Particle Size

This subsection reports a systematic variation of the size of fine AP particles in a wide range of sizes (approaching different orders of magnitude). Three ranges of AP size were employed: the 2, 10, and the 75-μm AP. Since the 2-μm AP was available only with HTPB, and in a mixture ratio of AP/binder = 65/35, for reasons explained earlier, all of the other test samples in this subsection also conform to these stipulations. The HTPB is cured with IPDI, which has reduced melt flow effects compared to DDI, the other diisocyanate curing agent studied in this work. 1% Pyrocat was used in the catalyzed samples. The matrix lamina thickness in the sandwiches is again ~250–275 μm, as in Sec. IV.E. The burning rates for matrix and sandwich are shown separately in Figs. 8a and 8b for the sake of clarity.

The uncatalyzed 2-μm AP matrix does not burn in the entire pressure range tested. Other uncatalyzed matrices burn only in the pressure ranges indicated in Fig. 8a. Note that the particle size effect on the uncatalyzed matrix is the reverse of the conventional trend of increasing burning rate with decreasing particle size. The 2- and 10-μm AP uncatalyzed sandwiches exhibit a mesa in the 1.04–3.5 MPa range, and a plateau in the 3.5–6.9 MPa range, and higher (not shown here), respectively (Fig. 8b). The uncatalyzed 75-μm AP sandwich curve also exhibits a relatively low exponent in the midpressure range (0.69–2.1 MPa). Such effects, explained as related to the relative length scales of lateral binder melt flow and fine AP particle size in the matrix,[30] are smeared by the presence of

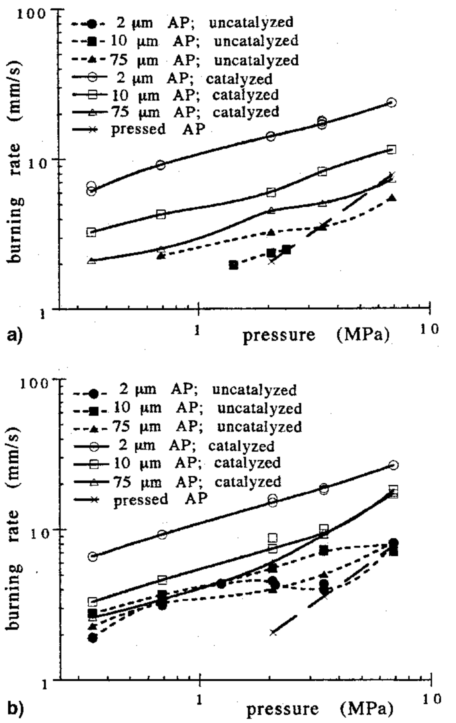

Fig. 8 Effect of fine AP particle size on the catalytic effect of 1% Pyrocat on samples with a matrix of AP/HTPB-IPDI = 65/35: a) matrix and b) sandwich burning rates.

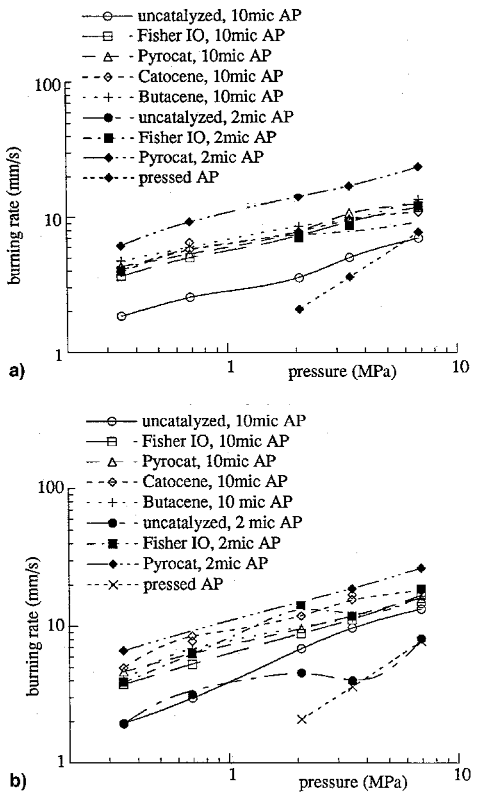

Fig. 9 Effect of dispersion ability of iron catalysts on the burning rate catalysis of AP/HTPB-IPDI samples: a) matrix and b) sandwich.

the catalyst. As for the effect of AP particle size on the catalysis, the 2-μm AP samples clearly register the highest catalytic effect, followed by the 10- and 75-μm AP samples. The effect is clearer in matrices than in sandwiches; the differences in the particle-size dependence of the catalytic effect in the sandwiches is diminished, particularly between that of the 10- and 75-μm AP sandwiches and at higher pressures. Similar AP particle size effects on catalysis are also reported in the literature.[9] Also, the conventional trend of increasing burning rate with decreasing particle size is restored in the presence of the catalyst.[7]

G. Effect of Dispersibility of the Catalyst

Four different iron-containing catalysts were chosen to investigate the effect of the degree and scale of dispersion of the catalyst in the binder: 1) Fisher Fe_2O_3, particle size ~1 μm (larger than Pyrocat); 2) Pyrocat; 3) Catocene, a liquid catalyst; and 4) Butacene®, a specialty resin, produced by SNPE, France, in which a ferrocenic silane group is grafted to the backbone of the HTPB molecule.[32]

1. HSM Observations

Both Fisher and Pyrocat IO are rust colored and turn black at ~200°C; no further changes are observed up to ~900°C. Catocene vaporizes at ~360°C, leaving a fine bed of black particulate residue. Butacene (uncured) vaporizes between 470-500°C, just as HTPB prepolymer would, leaving a residue similar to that left by Catocene. A blend of HTPB:Butacene = 62:38 cured by IPDI behaves similarly to HTPB binder without Butacene; it slowly melts at ~300-360°C, and boils at 480-500°C, but leaves a residue characteristic of uncured Butacene, as opposed to no significant residue for HTPB with no catalyst.[31]

2. Burning Rate Measurements

Two sets of tests were performed. In the first set, all the four iron catalysts were used in combination with 10-μm AP in the matrix. The IO particulate catalysts were added at the 1% level, and 2% Catocene was used as in typical rocket propellants, twice as much Catocene is generally used as the amount of IO to roughly equalize the iron content[24] (the exact equivalent amount is slightly more than 2% in an AP/binder = 7/3 mixture). Butacene has an average iron content of approximately 7.8% by weight. A blend of HTPB:Butacene = 62:38 was used to obtain an iron content that is equivalent to the other catalyzed mixtures. For the sake of compatibility with the Butacene tests, HTPB was chosen as binder in the other tests where the catalyst was externally added. Again, IPDI was chosen as the curative to have reduced binder melt flow effects. The matrix is a mixture of 10-μm AP and HTPB-IPDI in the ratio of 7/3. Matrix lamina thickness in all sandwiches is ~250-275 μm, corresponding to maximum burning rates in Fig. 2, as in Secs. IV.E and IV.F.

The results are presented as part of Figs. 9a and 9b, as matrix and sandwich burning rates vs pressure, respectively. The sandwich rates are always slightly higher than the corresponding matrix rates, except for the Butacene samples at 0.345 MPa. Curves for the different catalysts are clustered in the case of matrix (similar results are reported in the literature[2,11]), and slightly spread out in the case of sandwich rates. In either case, the arrangement of the curves does not directly correlate to the extent of dispersion of the catalyst in the binder.

The second set of tests is on a smaller scale. Here, the Fisher IO was used at the 1% level in combination with the 2-μm AP in a matrix of AP/HTPB-IPDI = 65/35. The remaining parameters are the same as in the first case. This situation corresponds to comparable orders of magnitude for the particle sizes of the catalyst and the oxidizer. These results are also shown in Fig. 9. The Fisher IO matrix burns in the entire pressure range 0.345-6.9 MPa, in contrast to no deflagration by the uncatalyzed 2-μm AP matrix. The Fisher IO sandwich rates have a greater overall burning rate, but preserve the mesa exhibited by the corresponding uncatalyzed sandwich burning rate curve; this is in contrast with washout of plateau and mesa behavior with the addition of Pyrocat. In both the matrix and sandwich, the burning rates of the Fisher IO samples are significantly lower than those of Pyrocat samples at all of the pressures tested, registering a definite effect of the dispersibility of the catalyst when in combination with the 2-μm AP.

3. SEM Observations

Sandwiches, in Sec. IV.G.2, were quenched while burning by rapid depressurization, and the quenched surfaces were examined in the SEM. The relevant pictures are not presented here in the interests of economy of space, and because they are not too different from Fig. 3. In all of the cases, accumulation of the catalyst on the surface is evident. Qualitatively, the extent of accumulation varies from dense but sporadic clusters in the case of Fisher IO, to a more uniform web of thin filigrees in the case of Butacene. The overall matrix surface does not indicate any undulations at the locations of these clusters. Even in the case of the Fisher IO, the dense clusters are smaller than the fine AP particle size, so that any such undulations in the surface caused by them are smaller in length scale than those caused by the AP particles and, therefore, may go unnoticed.

V. Discussion

A. Perspective Based on Previous Studies

Earlier studies in the present project involved tests on sandwiches with outer AP laminae and either pure binder,[23] catalyzed binder,[6,7,24] or AP-filled binder[25,26] as the middle laminae. In these studies it was concluded that the exothermic reactions that controlled the sandwich burning rate were in the gas phase flames (LEFs), and that high burning rate resulted from close proximity of those flames to the burning surface. In the case of sandwiches with catalyzed binder, it was concluded that the catalyst acted at the binder surface by the breakdown of heavy fuel molecules into more reactive species, but that the dominant rate enhancement resulted from greater proximity of the O/F flames to the surface because of the more reactive fuel species. In the case of sandwiches with fine AP added to the binder, it was recognized that the contact area of AP and binder in the solid was enormously increased, posing the possibility of a significant increase in heat release in condensed phase, interfacial, and heterogeneous surface reactions, if any. However, the results suggested that gas phase flames (LLEFs and PLEFs/canopy premixed flames) still controlled the burning rate. In the present study, a catalyst was added to the AP-filled binder, providing greater opportunities for exothermic reactions associated with the greater proximity of the catalyst to O/F interfaces, oxidizer, and all vapors at the surface.

B. Opportunity for Catalytic Action at Different Sites in the Combustion Zone and Its Implications

When discussing the mechanism of catalytic enhancement of the burning rate in the present case, it is important to remember several physical aspects of the test samples and propellants in general, aspects often overlooked in past studies on burning rate catalysis. Items 1–5, shown next, roughly pertain to the condensed phase, items 6–10 pertain to the surface layer, and items 11 and 12 pertain to the gas phase of the propellant combustion zone (Fig. 10).

1) The catalyst is present in test samples only in the binder, poorly situated to directly catalyze the oxidizer in the condensed phase.

2) The catalyst has the opportunity to affect the oxidizer in the condensed phase only at the oxidizer/binder interfacial surfaces.

3) The catalyst may be able to directly act on the binder in the condensed phase within the thermal wave.

4) Catalytic action in the condensed phase, on the binder, and/or at the interfacial surfaces, might a) be exothermic, b) accelerate the condensed phase decomposition of the ingredients, and/or c) alter the decomposition vapors, probably into a more reactive species. As for item a, catalytic action on conventional hydrocarbon binders is expected not to be exothermic, but catalyzed interfacial surface reactions might be. Exothermicity in the condensed phase is effective in terms of heat feedback and rate enhancement. An additional implication of such a mechanism is a relatively higher catalytic effectiveness at low pressures, and vice versa.[33] Item b would merely allow the surface of the ingredient that pyrolyzes faster to be recessed more,[34] without considerably affecting the burning rate. Item c is a potential mechanism because it would facilitate the gas phase flames being held closer to the burning surface, and thereby increase the burning rate.

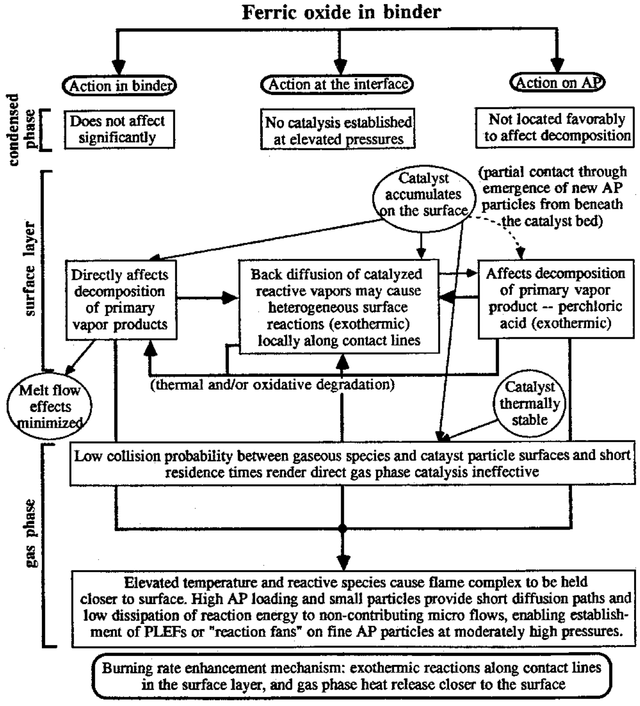

Fig. 10 Overview schematic of the mechanistic arguments for the action of ferric oxide in the combustion of AP composite propellants.

5) In considering factors that influence the burning rate, it is important not only to note sites of exothermic heat release, but also regions (usually) adjacent to those sites that are receptors of heat, but not contributors to local heat release. With fine oxidizer particles, the increase in the interfacial area facilitates enhanced thermal diffusion between oxidizer particles and adjacent binder layers, so that the heat generated at interfacial surfaces can be readily distributed uniformly into parts of the solid that do not directly participate in the local exothermic reactions.

6) The catalyst has been observed in the past,[2,6] and the present studies to concentrate on the binder surface, providing an enhanced opportunity for the breakdown of primary fuel decomposition products into more reactive vapor species.

7) With very small oxidizer particle size, the catalyst concentration may be encountered by some of the primary oxidizer vapors, raising the possibility of a catalyzed near-surface breakdown of some of those primary oxidizer product vapors. With AP oxidizer, it is quite likely that the catalyzed decomposition of $HClO_4$ is accompanied by exothermic heat release,[10] and more reactive oxidizer species.

8) With a very fine oxidizer, the diffusion distances for heterogeneous surface reactions are short, i.e., all oxidizer vapor is near fuel surfaces, and all fuel vapor is near oxidizer surfaces, increasing the possible role of vapor–surface O/F reactions. The presence of the catalyst can further enhance such reactions.

9) Besides the possibility noted in item 8, the opportunity exists for catalytic decomposition vapors of fuel and oxidizer to undergo gas phase (exothermic) reactions in the mixing region along the oxidizer/binder contact lines while diffusing to each other's surfaces.

10) Remarks about thermal diffusion in the solid made in item 5 are also pertinent to near-surface and heterogeneous reactions noted in items 6–9.

11) Fe_2O_3 is thermally stable up to ~1000°C (Ref. 9). Therefore, it would remain in condensed form in most of the combustion zone, except possibly as it enters the gas phase flame. Considering the low initial concentration of the catalyst in the propellant, and the fact that it accumulates on the surface, catalyst particles may, at best, be sporadically distributed in the gas phase at any instant of time. Thus, the catalyst does not have much opportunity to catalyze the LEF reactions directly because such flames are thin, and the opportunity for catalysis is small because of low collision probability with catalyst particles in the thin O/F flamelets. To the extent that direct flame catalysis might be present, one would expect the effect to be proportional to concentration used in the propellant, a corollary contrary to the test results (Fig. 2).[15] Thus, it seems that catalysis in the gas phase has a minimal role in influencing burning rate.

12) On the other hand, if the inclusion of the catalyst can result in exothermic heat release at or below the surface, and/or release more reactive fuel and oxidizer species into the gas phase, it can cause the gas phase flame complex to stand closer to the surface, and increase the burning rate correspondingly. It appears that this could potentially change the gas phase flame structure, the implications of which will be addressed later.

C. Present Results

The new results described in the last section indicate that the use of iron catalysts in the fine AP/binder matrix lamina produced a much larger enhancement in sandwich rates than did the addition of either catalyst[6,7,24] or AP alone[25,26] to the binder lamina. The catalyst also enhanced the rate of the matrix burning alone (Fig. 2a), and led to matrix burning under conditions for which the uncatalyzed matrix would not burn alone [binder melt + fine AP (Figs. 7 and 8), and more fuel-rich mixtures (Fig. 2b)]. The burning rates of sandwiches with catalyzed matrices were relatively insensitive to matrix lamina thickness (Fig. 2). All of these effects are indicative of an enhanced role for the matrix in determining the burning rate when the iron catalyst is present. The extent of the enhanced role for the catalyzed matrix appears to be dependent on the AP/binder mixture fraction and the size of the AP particles, but not on the dispersibility of the catalyst in the binder or the susceptibility of the binder to melt. The implications of these dependencies will be discussed next.

1. *Effect of Dispersibility of the Catalyst*

The different iron catalysts (dispersed differently in the binder) retain differences in their structural identity only beneath the surface, but all emerge as a fine bed of black particles accumulated on the surface (see Secs. IV.G.1 and IV.G.2). However, the dependence of the burning rate on the difference in the way the iron catalysts are dispersed beneath the surface is negligible (Fig. 9).[2,11] Iron atoms are contained in Fe_2O_3 when particulate catalysts are used, and in ferrocenic structures in Catocene and Butacene, with the latter being attached to binder molecules. Considering that catalytic effectiveness depends upon contact with AP oxidizer (discussed next), and assuming that the chemical mechanism of action of all these catalysts is fundamentally the same, it is unlikely that the different catalysts would have the same opportunity for action in the condensed phase. Furthermore, the pressure dependence of the matrix burning rate is preserved, even with the inclusion of the catalyst (e.g., Fig. 9a); in other words, there is an overall increase in burning rate with the catalyst present, without particular preference to any pressure level in the 0.69–6.9 MPa pressure range. To the contrary, any exothermicity in the condensed phase caused by the catalyst would result in a lower pressure exponent of the catalyzed matrix rate than the uncatalyzed matrix rate, i.e., more catalytic effectiveness at low pressure. These considerations indicate that the condensed phase is not the location of prominent action of the catalyst in the 0.69–6.9 MPa range. The catalytic effectiveness of the sandwich burning rates (Fig. 9b) weakens with an increase in pressure because of the increased predominance of the LLEFs in the uncatalyzed sandwiches at higher pressures. This indicates that catalysis of the LLEFs (by way of more reactive species) is probably not the primary mechanism controlling the burning rate of the catalyzed AP-filled binder sandwiches.

2. *Effect of Oxidizer Type*

The relatively weak (or negative) effect of the iron catalysts on burning rate with non-AP oxidizers (Fig. 6) indicates that either 1) the oxidizer–fuel reactions are not important contributors to heat flow to the surface, or 2) the non-AP oxidizer reactions are not catalyzed by iron catalysts. For instance, HMX/PBAN reactions are not considered as important, but KP/PBAN reactions are considered adequately exothermic to influence burning rate. The noneffect of Fe_2O_3 on KP-based samples (Fig. 6)[14,15] lends support to the view in 2. Among the oxidizers that were tested, AP was unique in that one of its two primary decomposition products is $HClO_4$. This gives rise to the possibility of a variety of heterogeneous and vapor phase reactions involving Fe_2O_3, some exothermic, such as 1) catalyzed decomposition of $HClO_4$ (Refs. 10, 13–15) (products of which may, in turn, accelerate binder destruction),[20] 2) catalysis of $HClO_4$ + binder → products,[21] and/or 3) the formation of thermally unstable intermediates such as iron perchlorate amines (with associated heat release).[10,18,22] With item 1, indeed, lighter fuel fragments are reported with finer AP particles.[9]

But recall that the catalyst is primarily in the binder. With fine AP particles, the opportunity for the catalyst concentration on the surface to come in contact with AP primary decomposition vapors along the AP/binder contact lines is enormous. Furthermore, the finer the dispersion of the catalyst in the binder, the more uniform the web of concentrated catalyst on the surface, allowing for the possibility of direct contact between the catalyst and new AP particles emerging on the surface from beneath the web. An immediate implication of such a scenario is that the catalyst may not be very effective if it is of comparable particle size to the oxidizer particles. This is indeed attested to by the results of this study (see Sec. IV.G.2, third paragraph).

3. *Effect of Fine AP Size*

Figure 8 clearly shows that the effect of Fe_2O_3 increases with a decrease in fine AP particle size. Since direct action of the catalyst in the condensed phase or gas phase is unlikely, as discussed previously, the remaining plausible scenarios that can explain this effect are: 1) increased catalytic action, gas phase and heterogeneous, along the contact lines between AP particles and the binder in the surface layer that are increased by decreasing particle size; and 2) attachment of gas phase PLEFs in the mixing fans arising from the contact lines of the AP particles, which may increase in number as a result of a decrease in particle size. Considering that Pyrocat is much finer than the smallest AP size tested (the 2-μm AP), the results in Fig. 8 strongly support the possibility in 1, as also suggested in the last paragraph. The possibility suggested in 2 is not mutually exclusive to that in 1; in other words, they can happen simultaneously. This will be addressed in some detail later. However, since the mixing distances in the gas phase would be very short for the 2-μm AP particles, it is unlikely that PLEFs can be attached before complete mixing takes place. But the catalytic effect is maximum with the 2-μm AP particles (Fig. 8). The possibility in 2 is speculative in view of this aspect.

4. *Effect of Binder Melt Flow*

The presence of binder melt flows 1) significantly affects the flammability of fuel-rich mixtures such as the matrices tested in this study, 2) reverses the trend of AP particle size effect on burning rate, and 3) is also strongly associated with the plateau and mesa burning behavior of sandwiches.[30] It is notable that the presence of iron catalysts tends to support combustion of fuel-rich mixtures, independent of the degree of susceptibility of the binder to melt (Fig. 7), re-establishes the particle size effect trend (Fig. 8), and eliminates the plateau-burning features attributed to melt flow (Figs. 7 and 8). The effect of binder melt flows can be better explained when the importance of the microscopic regions along fine AP/binder contact lines in the matrix is considered because this is the region where the melt flow is most intrusive on the adjacent AP particles. The present results suggest that the catalyst may initiate or catalyze exothermic reactions at sites aligned with the contact lines that accelerate the decomposition of binder melts that would otherwise flow onto AP surfaces and cause the anomalous effects listed earlier. Unfortunately, these three-dimensional microscopic details (e.g., of the 1-μm scale) are not resolvable in photography, and surface details appear to be obscured in quench tests by binder melt flow during or after flame quench (even for binders that are less susceptible to melt, e.g., PBAN).

The amount of heat release from these reactions may not be large because of the limitation on the availability of reactants at the reaction sites, but such reactions may be important because of the abundance of such reaction sites with the inclusion of fine AP particles, and their strategic location along contact lines close to or at the surface.

5. *Interpretation of Surface Features*

The catalytic exothermic reactions at the O/F contact lines would furnish hotter and more reactive vapor species for reaction at the gas phase flame (premixed or LEF). This is conducive to greater proximity of the flame complex to the surface than in the absence of the catalyst. The quenched surface features of catalyzed sandwiches (Figs. 3 and 4) may be explained based on the previous scenario. The enormity of interfacial contact in the fine AP/binder matrix lamina affords a net heat release sufficient to pyrolyze the matrix without having to cause lateral heat drain from the adjoining AP laminae, preventing retarded regression of the lamina AP immediately adjacent to the interface. The external heating of the lamina AP self-deflagration in the immediate vicinity of the interface edge by the LLEFs is speculated to cause the thin liquid layer on the deflagrating AP surface to dry up, resulting in a parched appearance of the surface in that region. (The smooth quality of the AP lamina in the corresponding region of an uncatalyzed sandwich is speculated to be caused by the dissociative sublimation of AP, owing to lateral heat loss to the binder/matrix lamina.[23]) The greater proximity of the LLEFs to the lamina interface edges (compared to the case of uncatalyzed sandwich) explains the smaller width of the dry band (when compared to the smooth band of the uncatalyzed sandwich).

D. Implications on the Gas Phase Flame Structure

The closer location of the overall flame complex would increase the temperature gradient in the gas phase and provide increased heat feedback to the surface, thereby causing the burning rate to increase. However, the details of how the gas phase flame above the fine AP/binder matrix lamina responds to exothermic reactions along the contact lines in the presence of the catalyst is not clear (because of the lack of direct observation). It appears that the catalyzed breakdown of both the binder and oxidizer primary decomposition products (the latter accompanied by heat release), would produce hotter and more reactive species (than without the catalyst) in the micro O/F mixing fans above the AP/binder contact lines, as mentioned earlier. It is not hard to visualize, then, the possibility of a buildup of subsequent exothermic O/F reactions along these mixing fans in a diffusion limited fashion. The limitations on such reactions are 1) the diffusion length scales dictated by AP particle size, the thickness of adjacent binder layers (governed by matrix mixture fraction), and the extent of peripheral contact between the oxidizer particles and the catalyst; and 2) upstream–lateral thermal diffusion from the mixing fans to adjacent nonparticipating species both in the gas phase and particularly in the condensed phase that needs to be pyrolyzed, again dictated by the same geometric factors as in 1. Such a three-dimensional mass and energy balance applied locally to these microscopic sites would, in reality, yield fairly low temperatures for reactions in the mixing fans in the immediate vicinity of the AP/binder contact lines on the surface. For this reason, such reaction fans attached to AP particles (if present) would not behave like conventional diffusion (Burke–Schumann) flames, but with an axially increasing temperature and reactivity (greatest along the stoichiometric contours in the mixing fans) in the immediate vicinity of the surface. If the catalytic action is less, or the upstream heat loss is greater, then reactivity near the surface would be less, and the reaction fans may be replaced by PLEFs. Under favorable conditions of high AP fraction and optimum (explained shortly) particle size in the matrix, it is quite possible that such reaction fans or PLEFs are established in the presence of the catalyst, whereas the corresponding uncatalyzed matrix may burn with a premixed canopy flame considerably far away from the surface. The reason for the optimum size stipulation is as follows: the finer the AP size, the greater the contact line density, the greater the total catalytic heat release at the contact lines, and the lesser the thermal burden on the reaction fans. Finer AP size also implies shorter diffusion distances, which means the reactants may mix completely before appreciable heat release above the contact lines, and burn in a premixed flame slightly farther away (still much closer than in the uncatalyzed case). Note that the optimum size stipulation is for the existence of reaction fans or PLEFs and is not to imply higher burning rates as being associated with reaction fans or PLEFs as opposed to a premixed flame. The following subsection is aimed at further clarifying the gas phase details.

In the case of an AP (10-μm)/PBAN = 5/5 matrix, the uncatalyzed matrix does not burn, whereas the catalyzed matrix sustains combustion in a smoldering fashion with low burning rates that exhibit negligible pressure dependence. In such a case, it is very likely that the heat loss to the excess binder precludes establishment of reaction fans or PLEFs, and the pyrolysis is barely sustained by the catalytic reactions along the AP/binder contact lines. When such a matrix is sandwiched between AP laminae, significant assistance is obtained by these surface-layer reactions from the LLEFs in the vicinity of the lamina interface edge, probably by way of an increased temperature at which to react. The result is a tremendous jump in the burning rate for the sandwiches when compared to the matrix burning alone (Fig. 2b). The sandwich surface profile also exhibits a conspicuous protrusion of the central portion of a very thick matrix lamina (Fig. 5a), commensurate with such a hypothesis.

In the case of the sandwiches with catalyzed 10-μm AP/PBAN = 7/3 matrix, there is no protrusion of the matrix lamina (Fig. 5b). In such a situation, it is not clear whether the matrix burning proceeds with a premixed flame or with PLEFs/reaction fans; the AP loading and particle sizes are not unfavorable for the establishment of PLEFs or reaction fans. Recall that the uncatalyzed 7/3 matrix is expected to burn with a premixed flame at the pressures tested.[26] However, since the PLEFs or reaction fans in the catalyzed matrix would be closer to the surface than the LLEFs above the lamina interface edges (owing to the catalytic action), it is likely that a matrix (alone) with PLEFs or reaction fans burns just as fast as, or faster than, its corresponding sandwich. The results of this study are contrary to such an expectation, i.e., the sandwich rates are almost always greater than the corresponding matrix rates for the present test variables. Therefore, the matrix lamina in these tests most probably burns with a premixed flame, held closer to the surface (along with the LLEFs) than in the uncatalyzed case. The LLEFs do not directly control the burning rate as in the uncatalyzed case, but do so in interaction with the catalytic reactions and the matrix gas phase flame (premixed or PLEF/reaction fan array). For this reason, the interaction between adjacent LLEFs is weakened relative to the matrix processes, and this is borne out by the weaker peaks in the burning rate vs matrix lamina thickness curves of the catalyzed sandwiches when compared to the corresponding uncatalyzed sandwich curves (Fig. 2).

VI. Conclusions

The results of the present study indicate that the Fe_2O_3 catalyst in AP/hydrocarbon binder propellants can act by multiple paths to increase the burning rate. As reported earlier,[6,7,24] the catalyst is located in the binder and concentrates on the surface, and is best suited to alter the fuel decomposition products. However, the present results with fine particulate oxidizer-filled matrices indicate that the catalyst enhances exothermic reactions at, and/or very close to the surface along the oxidizer-binder contact lines on the surface. These reactions become an increasingly important source of heat release and reactive fuel and oxidizer species as the density of contact lines increases with decreasing AP particle size and increasing proportion of AP in the AP/binder matrix.

Acknowledgments

This work was performed under Contract N00014-89-J-1293 with the U.S. Office of Naval Research, with Richard S. Miller as the Technical Monitor. Useful guidance was offered by Russell Reed, U.S. Naval Air Warfare Center, China Lake, California. Some ingredients used in this study were supplied by Woodward Waesche, Science Applications International Corp.; Carol Hinshaw and Robert Wardle, Thiokol Corporation; John Murphy, Elf Atochem North America, Inc.; and Elizabeth Katres, Hüls America, Inc.

References

[1] Kishore, K., and Sunitha, M. R., "Effect of Transition Metal Oxides on Decomposition and Deflagration of Composite Solid Propellant Systems: A Survey," *AIAA Journal*, Vol. 17, No. 10, 1979, pp. 1118–1125.

[2] Lengellé, G., Brulard, J., and Moutet, H., "Combustion Mechanisms of Composite Solid Propellants," *Proceedings of the 16th Symposium (International) on Combustion*, The Combustion Inst., Pittsburgh, PA, 1976, pp. 1257–1269.

[3] Handley, J. C., and Strahle, W. C., "Behavior of Several Catalysts in the Combustion of Solid Propellant Sandwiches," *AIAA Journal*, Vol. 13, No. 1, 1975, pp. 5, 6.

[4] Fong, C. W., and Hamshere, B. L., "The Mechanism of Burning Rate Catalysis in Composite HTPB—AP Propellant Combustion," *Combustion and Flame*, Vol. 65, 1986, pp. 61–69.

[5] Fong, C. W., and Hamshere, B. L., "The Mechanism of Burning Rate Catalysis in Composite Propellants by Transition Metal Complexes," *Combustion and Flame*, Vol. 65, 1986, pp. 71–78.

[6] Price, E. W., and Sambamurthi, J. K., "Mechanism of Burning Rate Enhancement by Ferric Oxide," *Proceedings of the 21st JANNAF Combustion Meeting*, Chemical Propulsion Information Agency, Publ. 412, Vol. 1, 1984.

[7] Price, E. W., Sambamurthi, J. K., and Sigman, R. K., "Further Results on the Combustion of AP/Polymer Sandwiches with Additives," *Proceedings of the 22nd JANNAF Combustion Meeting*, Chemical Propulsion Information Agency, Publ. 432, Vol. 1, 1985.

[8] Krishnan, S., and Jeenu, R., "Subatmospheric Burning Characteristics of AP/CTPB Composite Propellants with Burning Rate Modifiers," *Combustion and Flame*, Vol. 80, 1990, pp. 1–6.

[9] Krishnan, S., and Jeenu, R., "Combustion Characteristics of AP/HTPB Propellants with Burning Rate Modifiers," *Journal of Propulsion and Power*, Vol. 8, No. 4, 1992, pp. 748–755.

[10] Pearson, G. S., "The Role of Catalysts in the Ignition and Combustion of Solid Propellants," *Combustion Science and Technology*, Vol. 3, 1971, pp. 155–163.

[11] Bobolev, V. K., Gen, M. Y., Mal'tsev, V. M., Melesov, G. P., Pokhil, P. F., Seleznev, V. A., Stasenko, A. N., and Chuiko, S. V., "Mechanism of Action of Iron Catalysts on the Combustion of Composite Systems," *Fizika Goreniya i Vzryva*, Vol. 7, No. 3, 1971, pp. 366–375.

[12] Jones, H. E., and Strahle, W. C., "Effects of Copper Chromite and Iron Oxide Catalysts on AP/CTPB Sandwiches," *Proceedings of the 14th Symposium (International) on Combustion*, The Combustion Inst., Pittsburgh, PA, 1973, pp. 1287–1295.

[13] Ermolaev, B. S., Korotkov, A. I., and Frolov, Y. V., "Study of the Action of Catalysts Using Layered Systems," *Fizika Goreniya i Vzryva*, Vol. 5, No. 2, 1969, pp. 286–289.

[14] Pittman, C. U., Jr., "Location of Action of Burning-Rate Catalysts in Composite Propellant Combustion," *AIAA Journal*, Vol. 7, No. 2, 1969, pp. 328–334.

[15] Bakhman, N. N., Nikiforov, V. S., Avdyunin, V. I., Fogelzang, A. E., and Kichin, Y. S., "Catalytic Effect of Ferrous Oxide on Burning Rate of Condensed Mixtures," *Combustion and Flame*, Vol. 22, 1974, pp. 77–87.

[16] Strahle, W. C., Handley, J. C., and Milkie, T. T., "Catalytic Effects in the Combustion of AP-HTPB Sandwiches to 3200 PSIA," *Combustion Science and Technology*, Vol. 8, 1974, pp. 297–304.

[17] Boggs, T. L., Zurn, D. E., Cordes, H. F., and Covino, J., "Combustion of Ammonium Perchlorate with Various Inorganic Additives," *Journal of Propulsion and Power*, Vol. 4, No. 1, 1988, pp. 27–40.

[18] Kishore, K., and Sunitha, M. R., "Mechanism of Catalytic Activity of Transition Metal Oxides on Solid Propellant Burning Rate," *Combustion and Flame*, Vol. 33, 1978, pp. 311–314.

[19] Krishnan, S., and Periasamy, C., "Low-Pressure Burning of Catalyzed Composite Propellants," *AIAA Journal*, Vol. 24, No. 10, 1986, pp. 1670–1675.

[20] Korobeinichev, O. P., Anisiforov, G. I., and Tereschenko, A. G., "High-Temperature Decomposition of Ammonium Perchlorate-Polystyrene-Catalyst Mixtures," *AIAA Journal*, Vol. 13, No. 5, 1975, pp. 628–633.

[21] Korobeinichev, O. P., Kovalenko, K. K., and Lesnikovich, A. I., "Investigation of Effect of Oxide and Organometallic Catalysts on Thermal Decomposition and Combustion of a Model Ammonium Perchlorate-Polymer System," Plenum, New York, 1978.

[22] Kishore, K., Pai Verneker, V. R., and Sunitha, M. R., "Action of Transition Metal Oxides on Composite Solid Propellants," *AIAA Journal*, Vol. 18, No. 11, 1980, pp. 1404, 1405.

[23] Price, E. W., Sambamurthi, J. K., Sigman, R. K., and Panyam, R. R., "Combustion of Ammonium Perchlorate-Polymer Sandwiches," *Combustion and Flame*, Vol. 63, 1986, pp. 381–413.

[24] Markou, C. P, "Effect of Different Binders and Additives on Sandwich Burning," Ph.D. Dissertation, Georgia Inst. of Technology, Atlanta, GA, May 1988.

[25] Lee, S.-T., "Multidimensional Effects in Composite Propellant Combustion," Ph.D. Dissertation, Georgia Inst. of Technology, Atlanta, GA, May 1991.

[26] Lee, S.-T., Price, E. W., and Sigman, R. K., "Effect of Multidimensional Flamelets in Composite Propellant Combustion," *Journal of Propulsion and Power*, Vol. 10, No. 6, 1994, pp. 761–768.

[27] Price, E. W., "Effect of Multidimensional Flamelets in Composite Propellant Combustion," *Journal of Propulsion and Power*, Vol. 11, No. 4, 1995, pp. 717–728.

[28] Prasad, K., and Price, E. W., "A Numerical Study of the Leading Edge of Laminar Diffusion Flames," *Combustion and Flame*, Vol. 90, 1992, pp. 155–173.

[29] Fenn, J. B., "A Phalanx Flame Model for the Combustion of Composite Solid Propellants," *Combustion and Flame*, Vol. 12, June 1968, pp. 201–216.

[30] Chakravarthy, S. R., Price, E. W., and Sigman, R. K., "Binder Melt Flow Effects in the Combustion of AP-HC Composite Solid Propellants," AIAA Paper 95-2710, July 1995.

[31] Price, E. W., Chakravarthy, S. R., Zachary, E. K., and Sigman, R. K., "Ingredient Response and Interaction During Heating on a Hot Stage Microscope," *Proceedings of the 31st JANNAF Combustion Meeting*, Chemical Propulsion Information Agency, Publ. 620, Oct. 1994.

[32] Chen, J. K., Cheng, S. S., and Chou, S. C., "DSC, TG and Infrared Spectroscopic Studies of HTPB and Butacene Propellant Polymers," AIAA Paper 94-3176, June 1994.

[33] Krishnan, S., and Jeenu, R., "A Surface Reaction Model for Catalyzed Composite Propellants," *AIAA Journal*, Vol. 30, No. 11, 1992, pp. 2788–2791.

[34] Deur, J. M., and Price, E. W., "Steady State One-Dimensional Pyrolysis of Oxidizer-Binder Laminates," AIAA Paper 86-1446, June 1986.