JOURNAL OF PROPULSION AND POWER
Vol. 25, No. 5, September–October 2009

Nano Additives and Plateau Burning Rates of Ammonium-Perchlorate-Based Composite Solid Propellants

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DOI: 10.2514/1.40831

Plateau propellants exhibit burning rate curves that do not follow the typical linear relationship between burning rate and pressure when plotted on a log–log scale, and because of this deviation, their burning behavior is classified as anomalous burning. This paper contains a literature review chronicling the last half-century of research to better understand the mechanisms that govern anomalous burning and to shed light on current research into plateau and related propellants. In addition to the review, a series of experiments investigating the use of nanoscale TiO_2-based additives in ammonium-perchlorate hydroxyl-terminated polybutadiene composite propellants was performed. The baseline propellant consisted of either 70 or 80% monomodal ammonium perchlorate (223 μm) and 30 or 20% binder composed of isophorone-diisocyanate-cured hydroxyl-terminated polybutadiene with Tepanol. Propellants were tested using a strand bomb between 3.45 and 17.24 MPa (34.0–170.1 atm). Analysis of the burning rate data shows that the crystal phase and synthesis method of the TiO_2 additive are influential to plateau tailoring and to the apparent effectiveness of the additive in altering the burning rate of the composite propellant. Some of the discrepancy in the literature regarding the effectiveness of TiO_2 as a tailoring additive may be due to differences in how the additive was produced. Doping the TiO_2 with small amounts of metallic elements (Al, Fe, or Gd) showed additional effects on the burning rate that depend on the doping material and the amount of the dopant. This work provides the first published propellant mixtures and burning rate results for composite propellants employing metal-doped nanoparticle additives.

I. Introduction

THE ability to tailor the burning rate of solid propellants has been a main driving force within the industry ever since it was determined that propellant burning rate can be modified through alterations to the propellant formula and/or through the use of various additives. During steady-state operations, traditional propellants follow a direct relationship between burning rate and pressure (only when plotted on a log–log graph) so that as one increases, so does the other. However, there are some propellant formulas that provide a distinct step away from this linear behavior and enable much more exotic relationships with pressure. This alternative class of propellant was first coined as having an anomalous-burning behavior because of the way the propellant burning rates departed from the norm. One of the more prominent versions of these anomalous-burning rates is known as plateau burning; this type of burning rate curve is the most common version of nonlinear relationships in modern propellants. A propellant that exhibits plateau burning has a pressure region in which the burning rate stabilizes and remains nearly independent of changes in pressure. Outside of this plateau region, the logarithm of the burning rate has a typical linear relationship with the logarithm of the pressure.

This study was designed to fulfill two objectives: first, to provide an extensive literature review on works that have contributed to understanding or creating plateau-burning curves, and second, to investigate the use of nanoscale additives in propellants that exhibit plateau burning. Only steady-state operations of composite propellants were considered in these objectives.

II. Background

The direct study of anomalous-burning composite propellants has been an ongoing research topic for nearly half a century. The mechanisms responsible for the anomalous-burning rates can be divided into three categories: binder melt layer, oxidizer behavior, and additive influences. This literature review looks at these three parameters in a historical approach following works that contributed to the observation and understanding of anomalous-burning rates. The present review is the first to provide an inclusive look at the groups and individuals that contributed to anomalous burning and to, in turn, discuss each group's or individual's specific contribution and related work. In effect, this is the first publication that shows the evolution of the mechanism(s) controlling anomalous burning and allows insights and interpretations of earlier work that was not possible at the time. It is also the desire of the authors that readers can use this summary to draw their own thoughts and focus new research within the subject. With regard to the authors' own work, such a review was needed so that their work on burning-rate-tailoring additives could be put into perspective relative to established observations of anomalous burning.

A. Binder Melt Layer

One of the earliest groups to publish on the phenomenon of plateau burning within composite propellants was the work done by Steinz et al. [1] at Princeton University throughout the 1960s. While working on an early one-dimensional model for composite

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Presented as Paper 4790 at the 44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, Hartford, CT, 21–23 July 2008; received 5 September 2008; revision received 31 March 2009; accepted for publication 19 April 2009.

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propellant combustion known as the granular diffusion flame model, Steinz et al. proposed several instrumental deductions on the cause of plateau burning as well as multiple significant observations. Plateau burning already existed and was widely seen in the propellant industry, as evident by an early NASA report on propellant selection [2], but lacked published evidence in the composite propellant field. One of the key statements proposed by Steinz et al. [1] was the theory that plateau burning was related to two other unusual burning behaviors of composite propellants: mesa burning and intermittent extinctions; all three of these behaviors became grouped together and labeled as anomalous-burning behaviors (sometimes referred to as abnormal burning).

As illustrated in Fig. 1, mesa burning is similar to plateau burning, but instead of the burning rate leveling off, it takes a distinctly negative slope to which the propellant may either recover into the usual positive linear climb or result in an extinction point. Intermittent extinction propellants typically appear as plateau propellants that simply will not burn during a specific pressure region, but elsewhere resemble typical burning characteristics. Burning curves during steady-state operations are traditionally described by the following equation in which r_b is the burning rate, P is the chamber pressure, a is an empirical coefficient based on initial grain temperature and other factors, and n is known as the pressure exponent [3]:

$$r_b = aP^n$$

Plateau regions typically have pressure exponent values near zero, and mesa regions are described by negative pressure exponents; often times, mesa propellants are simply referred to as negative-exponent propellants. Steinz et al. [1] first decided that these three behaviors were created by the same mechanism that destabilized and weakened the propellant combustion: at low levels, it would create a plateau; at higher levels, a mesa would form; and at the extreme, the mechanism would extinguish the propellant, causing intermittent extinction. Steinz et al. then defined the mechanism as the binder melt layer on the burning surface created by the liquefied fuel binder. This simple explanation, in a general sense, still stands today as the dominant reason hypothesized for such burning behaviors. Over the next four decades (and presently continuing on) the understanding of this mechanism has been greatly investigated and added upon.

Steinz et al. [1] also correlated binder types to different melt-layer attributes. They stated that binders that readily melt, such as polyurethane (PU) and polystyrene, would create the most anomalous behavior, but binders that are relatively harder to melt, such as polybutadiene acrylic acid (PBAA) and polybutadiene acrylonitrile acrylic acid (PBAN), still proved to be able to produce such behaviors, if to a more limited degree. In their work, several of these binders showed anomalous burning in ranges from 0.69 to 10.34 MPa (6.8 to 102.1 atm).

Boggs et al. [4] presented scanning electron microscope (SEM) observations of extinguished burning surfaces of ammonium perchlorate (AP)-based propellants; similar work was presented by Derr and Boggs [5]. These studies focused mostly on AP-PU propellants, but also explored carboxy-terminated polybutadiene (CTPB) binders to a limited degree and potassium perchlorate (KP) and cyclotetramethylene tetranitramine (HMX) as oxidizers. The PU binders studied only burned, at the most, up to 4.14 MPa (40.8 atm), and some showed unsteady burning below 0.69 MPa (6.8 atm). Boggs and Kraeutle [6] confirmed Steinz et al.'s [1] fluid binder explanation by visually observing binder melt evidence in the SEM images. Cinephotomicrography was also used to visually observe the melted binder, which was described as "the presence of a bubbling-liquid material on the burning surface" [5], although no images were published.

Notably in the PU-AP propellants, which were composed of 26% binder and showed upper deflagration limits no matter what AP size was used (8, 50, and 200 μm), it was seen that the binder level regressed faster than the AP at lower pressures, but at higher pressures, the AP regression rate eventually surpassed that of the binder. When the AP burned even with or below the binder in elevation, the liquid PU would eventually cover the AP, thus inhibiting its decomposition and deflagration. This concept is illustrated by Fig. 2, in which the AP particles only become submerged by the melt layer when the particles have decomposed below the binder surface, as shown on the right side of the diagram. The CTPB-AP propellant showed little evidence of melted surface flow, but still did show evidence of the binder burning faster than the AP, resulting in the AP particles protruding slightly above the binder at 4.14 MPa (40.8 atm), which was the only pressure observed. The use of SEM for propellants was also briefly discussed, which included the use of a gold-palladium coating that was required to be sputtered on the samples for use in the electron beam of the SEM; the cracks or fissures that appeared in the binder region of the samples were attributed to the cracking of this thin metallic coating. This work did great justice in validating Steinz et al.'s [1] explanation and set forth the need to better understand the binder in the propellant structure.

Varney and Strahle [7] at Georgia Institute of Technology conducted two-dimensional sandwich studies exploring a wide range of binders consisting of PU, polysulfide, PBAA, and CTPB, primarily by observing SEM images of extinguished surfaces. Sandwich tests, such as those of Varney and Strahle, investigate propellant combustion by structuring individual laminas of binder and fuel together, creating a two-dimensional simplification of an actual propellant. Observations proved that binder melt layers were being seen for all binders at all pressures tested, up to 16.55 MPa (164.3 atm), with various effects on the AP particles. The maximum point of regression on the sandwich surfaces was always seen in an AP lamina when tested at high pressures and seemed to be influenced by the extent of the binder melt flow on the AP surface.

After the mid-1970s, the industry also started to focus research into anomalous burning. However, the full extent of information withheld as proprietary in nature can only be speculated, at best. Cohen et al. [8,9] of Aerojet Solid Propulsion Company released reports on gas generators that used negative-exponent propellants. A propellant with an n value of −2.5 was described as a "practical negative exponent propellant" [8]. Later, burning rate plots were given for AP-PU propellants with and without aluminum (Al),

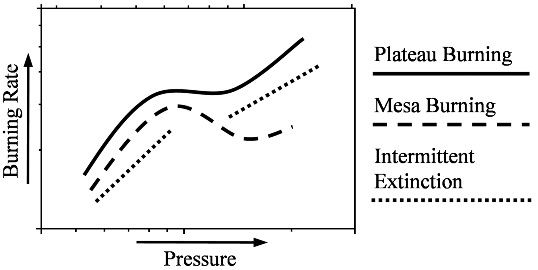

Fig. 1 The three types of anomalous burning. In plateau burning, the burning rate levels off over a pressure range. In mesa burning, the burning rate is inversely proportional to the pressure over a specific range. In intermittent extinction burning, the propellant is unable to sustain burning over a range of pressures.

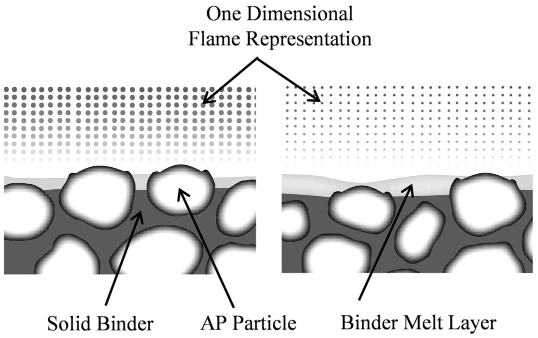

Fig. 2 Conceptual diagram of binder melt layer in a basic composite propellant using a one-dimensional flame representation. When the melt layer is near level with the AP, normal burning takes place (left), but when the AP burns faster than the melt layer, then the AP can become submerged (right).

displaying strong mesas and plateaus at the 2.76–6.89 MPa (27.2–68.0 atm) range.

Schmidt and Poynter [10], also of Aerojet Solid Propulsion Company, published work in 1980 focusing on metal particle combustion, but revealed several important characteristics of propellant binders, notably concerning hydroxyl-terminated polybutadiene (HTPB). Often times, liquid additives are mixed into binders to help create improved propellant mechanical properties and particle-to-binder bonding and to adjust curing characteristics [3,11]. In this study, two plasticizers, dioctyl adipate (DOA) and isodecyl pelargonate, and three curatives, isophorone diisocyanate (IPDI), dimeryl diisocyanate (DDI), and toluene diisocyanate (TDI), were tested and showed an ability to tailor anomalous-burning regions. Results showed that DOA and DDI could significantly increase the suppression level of propellant burning. These data provided the interest in scrutinizing not only the main polymer of the binder, but all constituents with regard to melt-layer properties, as indicated by later studies.

A group from Purdue University [12] studied curative effects in burning rate and SEM imaging of extinguished surfaces. Again, DDI and IPDI binders were compared in HTPB-AP propellants with bimodal (35:52 and 400/20 μm) oxidizer particles at an 87% solids loading. The binders also contained the additive Ag white at a 2% level. Very little discussion was presented with the findings, but even so, the previous trends of these two curatives seen by Schmidt and Poynter [10] were verified. However, this time, the DDI propellants did not fully extinguish, but just produced lower overall burning rates. This different result could have been because of an increased AP loading or due to the binder additive used by Frederick et al. [12]. Using the expressions formulated by Xu et al. [13], Frederick et al. [12] emphasized the need to quantitatively determine the AP surface area covered by molten binder at various pressures.

Cohen (now of Cohen Professional Services) and Hightower (at Thiokol Corporation) [14] published a paper in which addressing and explaining plateau burning was the main focus. In their report, an extensive review and comparison of Miller's [15,16], Foster and Miller's [17], Foster et al.'s [18], and King's [19] propellants, which are discussed later in their respective sections herein, were conducted and expounded upon, also providing additional plasticizer and solid additive comparisons. This publication was the first to put great emphasis on binder melt viscosity rather than just thickness. In a model calculation based on the steady-state heat conduction within the binder, the melt layer was plotted as a function of binder regression rate and surface temperature. The relationship revealed that at low temperatures (527–627°C), the binder can be as thick as 12 μm and would reduce to 3 μm or less above 777°C; these temperatures correlated well to regression rates of 0.2 in./s (5.1 mm/s) and 1.0 in./s (25.4 mm/s), respectively.

Cohen and Hightower [14] also considered the surface structure geometry that had been reported by the SEM observations made by the multiple groups previously discussed. Cohen and Hightower asserted that these two mechanisms alone, melt-layer thickness and surface structure, do not fully explain the anomalous burning. They suggested that the melt-layer viscosity was the missing piece of the puzzle. By using commercial oils as an analogy, it was shown that hydrocarbon liquids could potentially reduce their viscosity to that of water by heating to just a few hundred degrees Celsius. This behavior was well known in HTPB and other propellant binder polymers, as proven by the industry mixing standard, which entails heating the propellant ingredients while mixing to aid in the removal of air pockets and to increase mixing homogeneity [11].

By coupling melt-layer thickness and viscosity, the plateau phenomenon could be explained as starting when the viscosity reduced to a point at which the melt layer could flow over the AP particle, given that the surface structure permits this to happen, and ending when the melt layer would become too thin. From other observations, Cohen and Hightower [14] deduced that plasticizers reduce the binder viscosity, thus encouraging anomalous burning. This 1992 publication claims that the work "places the role of binder in solid propellant combustion in a new light" and that the "melt layer interference appears to be more prevalent than previously thought" [14]. Over two decades after Steinz et al.'s [1] original work, binder suppression of the oxidizer was still viewed as an unexplored phenomenon.

Klager and Zimmerman [20] of GenCorp/Aerojet Solid Propulsion Company authored an extensive review on burning-rate-tailoring parameters that had several mentions of anomalous burning. In this work, anomalous propellants are described to inherently exhibit very low πk values, which relate the initial temperature of the propellant grain to changes in the pressure of the motor chamber, and were credited with producing "a lightweight rocket motor...with benefits such as higher specific impulse, more neutral pressure-time curves, more safe conditions to minimum pressure fluctuations, and constant area ratio" [20]. The majority of data presented in this work depended on additives for anomalous burning and are further discussed in the additive review.

All of these groups have contributed to the overall understanding and characterization of the melted layer of the binder in composite propellants. They have shown that the interruption of AP combustion is highly influenced by the melt layer's presence, viscosity, and the relative level between the two surfaces. Different binders, and the curatives with which they are solidified, have been seen to have different melting properties, creating strong correlations between specific binders and anomalous burning. Other ingredients in the binder, such as plasticizers, can also be attributed to an increased melt layer. It was also observed that scaling propellant testing from strands to motors can alter the behavior seen in anomalous-burning curves. Even though binder flow has been qualitatively recorded to great lengths, an immense need for quantitative data still exists.

B. Oxidizer Contributions

In Steinz et al.'s [1] 1968 discussion of anomalous burning, it was noticed that certain oxidizer trends contributed to the abnormal burning, in addition to the effects of the molten binder. The observations made were that anomalous burning occurred most often at low AP loading and when the AP size was either extremely small or large or a mixture of the two.

In 1969, Boggs [21] released his four-regime description of the deflagration of single-crystal AP. The plot presented describing these four distinct pressure regimes is recreated in Fig. 3; here, it can be seen that AP will not sustain deflagration below 2.07 MPa. Boggs coupled these deflagration rates with SEM images of extinguished samples to describe the distinctly different physical surface structures of the separate regions, which enabled greater understanding of the nature of AP across a broad pressure range [6].

The significance of these data to plateau burning continues to be a point of speculation. Region III, as described by Boggs [21], was of highest interest to anomalous burning because of the sharp reduction in the AP deflagration, most likely due to the unsteady gas-phase flame causing the AP to be deprived of a steady thermal energy feedback, which is necessary for deflagration. In 1972, Varney and Strahle [7] postulated that the binder/oxidizer diffusion flame

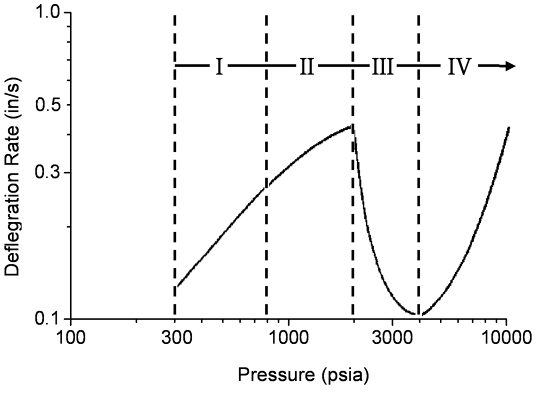

Fig. 3 AP Deflagration rates divided into the four regimes as defined by Boggs [21], taken directly from [21].

provides the steady thermal energy feedback necessary to sustain a positive increase in AP burning during region III. However, for anomalous-burning propellants that may not have a steady diffusion flame, the reduced AP deflagration rate could greatly affect propellant burning. Boggs [21] also noted that extinguished AP showed evidence of a molten froth layer on the surface that would manifest as a burst or vented bubble on the AP surface, the rupture being caused by the depressurization technique used to extinguish the sample. The molten layer was also noted to thin with rising pressure until during region II, in which the froth would become confined to valleys on the AP surface and eventually disappear.

At the beginning of the 1970s, Beckstead et al. [22] at Lockheed Propulsion published their famous model based on multiple flames, commonly referred to as the BDP (Beckstead–Derr–Price) model. This model is still used as the backbone for several modern propellant simulation efforts. Instead of looking at the propellant combustion as a single one-dimensional process, this model considered three separate flame structures that worked together. The oxidizer had a monopropellant flame directly overhead, a primary flame existed near the surface interface of the oxidizer and fuel, and a final diffusion flame existed further away from the burning surface, where the products of the previous flames would mix and combust; this can be seen visually in Fig. 4. The conceptual illustration created earlier (Fig. 2) can be recreated with the adaptation of this new flame geometry and can be seen in Fig. 5. Here, the BDP multiple-flame structure can be seen represented over the AP particles. The consequences of the binder melt layer can be seen to have far more drastic consequences than in a one-dimensional flame model; in this situation, not only is diffusion affected, but the heat flux created within the flame is also affected.

Cohen et al. [23], then at Lockheed Propulsion, were one of the first groups that did a great deal of work to better catalog the physical parameters of the various binders. Through surface pyrolysis data, they were able to define multiple physical properties of various binder systems and used them to improve the reporting of the BDP model. This effort included a broad range of binders, including PU, fluorocarbon, CTPB, PBAN, and HTPB; the last of which has become the predominant binder material in current propellants and in the present work.

At the Institute of Chemical Physics Academy of Sciences in the USSR, Glaskova [24] was conducting studies on additives that could inhibit AP combustion by chemical kinetic mechanisms. Even though these inhibitors achieved anomalous-burning rates in the AP self-deflagration curve, no application to creating a propellant was conducted. Nonetheless, the potential still exists to manipulate the propellant burning rate by the use of an additive that interacts directly with the oxidizer.

From Hercules, Inc., Miller [15,16] released several informative papers throughout the late 1970s through early 1980s cataloging the burning rate curves of dozens of propellants. In Miller's work, the next major direct guideline for anomalous-burning propellants was conceived: the need for a wide distribution of AP particle size; more precisely, the need for a multimodal distribution with small, fine sizes and correspondingly much larger, coarse sizes. This work supplied valuable comparisons of monomodal formulas (6, 20, and 200 μm), bimodal formulas with both fine size distributions (6/20 μm), and formulas consisting of the wide distributions in a trimodal fashion (2/20/400 μm).

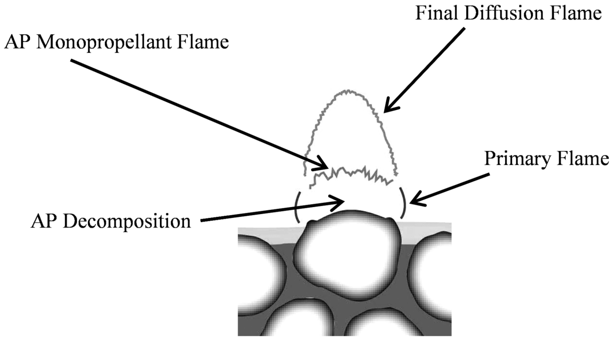

Fig. 4 Conceptual description of the multiple-flame (BDP) model first proposed by Beckstead et al. [22].

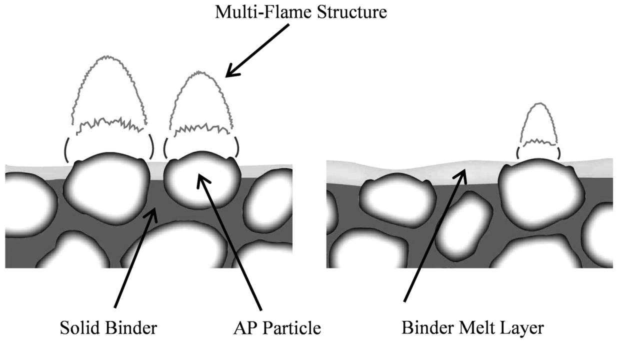

Fig. 5 A conceptual schematic showing the binder melt layer illustrated with the BDP multiple-flame model. Normal burning (left) shows the heterogeneous nature of this combustion. Binder melt layer interference of AP combustion (right) can be seen to have a significant impact on localized flames in this model.

Foster and Miller [17] and Foster et al. [18] supplemented this work with studies looking further at various oxidizer sizes and loadings, finding favorable conditions for anomalous burning, most notably above 6.89 MPa (68.0 atm) with very fine AP sizes in 75% AP.

Xu et al. [13] from Northwestern Polytechnical University in the People's Republic of China developed a model based on the BDP structure that attempted to include the binder melt mechanism to accurately predict the various types of anomalous burning. The main addition was a term that created a ratio of the AP surface covered by molten binder to uncovered AP surface area. This step was vital in enabling the BDP model to accurately predict anomalous burning.

At the Defence Research Centre in Salisbury, Australia, Fong and Smith [25] released a paper focusing on wide-distribution AP formulas directly corresponding to their ability to produce plateau-burning-rate curves. Using a statistical technique, the burning rate data from 22 bimodal and trimodal propellants were used to model the burning rate curves of pseudopropellants (analytically simulated propellants). The specific curative type used in the HTPB binder was not given, nor was the identity of a metal catalyst added at 0.5%; the AP loading was defined to be 82.5%. It was likely that the catalyst was copper-based, because Fong and Hamshere [26] were involved in publishing work on such catalysts during this time period. The plateaus seen were in the 6.89–13.79 MPa (68–136.1 atm) pressure region and showed no distinct mesas or extinction points. Building upon Miller's [15,16] previous work on wide AP distributions, Fong and Smith [25] observed that coarse-to-fine oxidizer ratios of 60:40 or greater had a higher chance of producing a plateau-burning propellant. The pseudopropellants accurately predicted previously published data for fine AP sizes, but the coarse AP sizes resulted in pressure independence, which was contrary to previous data; the existence of the melt layer was given as the main cause of the contradiction.

At the same time during the mid-1980s, Price et al. [27] from the Georgia Institute of Technology were fine-tuning the detailed structure of AP-binder flames by studying sandwiches of AP and PBAN propellants. This work continued throughout the 1980s and into the 1990s, when the group started investigating anomalous-burning mechanisms by using the sandwich techniques they had mastered. Papers published by this group all have extensive discussions that hold rich details of individual tests and offer great insight and intricacies into propellant burning [28–30]. The group correlated anomalous burning with the use of fine-sized AP and so focused work on matrices, that is, monomodal oxidizer/binder mixtures made to represent the portion of propellant structure between coarse oxidizer particles. Using these matrices, a large amount of data was cataloged, showing burning limits for various AP particle sizes from atmospheric pressure up to 13.79 MPa (136.1 atm). Price [29] also detailed how the melt flow interference correlates to the flame structure detailed in his earlier works. Data were also presented that showed melting temperatures for various binder systems by use of a hot-stage microscope; DDI-cured HTPB melted at 260°C, whereas IPDI-cured HTPB melted at 330–370°C, and PBAN melted at 480°C [31].

In 2007, Banerjee and Chakravarthy [32] at the Indian Institute of Technology conducted work that focused on the size of the coarse AP used in plateau-burning propellants. After defining burnable limits for the fine AP matrices used, coarse AP particles were tested ranging from 100–550 μm in diameter. It was found that larger sizes would shift a low-level plateau in the 3.00–8.00 MPa (29.6–78.9 atm) pressure range farther into lower pressures.

Through these works, several insights into the oxidizer's influences on anomalous burning have been achieved. Low oxidizer loading levels and smaller particle sizes were demonstrated to have a greater chance of producing an abnormal-burning curve. Plateau propellants in particular were shown to be produced by the use of a wide AP distribution that was found to work best at a 60:40, or greater, coarse-to-fine ratio. As indicated by most propellant models, oxidizers play a key role in propellant burning, and their role in anomalous burning may still not be fully understood.

C. Additive Influences

Additives have also been seen to influence the occurrence and intensity of anomalous burning. For example, while conducting propellant research by using two-dimensional sandwiches in the early 1970s, Strahle et al. [33] and Handley and Strahle [34] studied four different catalysts: ferrocene, iron blue, ferric oxide, and copper chromite ($Cu_2Cr_2O_5$, identified here as the Harshaw catalyst Cu 0202). In addition to finding that the catalysts created a greater increase to the overall burning rate when mixed into the pressed AP pellets and that iron blue and ferrocene led to the largest increase in burning rate, several important binder-related observations were made. It was seen that when the catalysts were mixed directly into the binder, the melt layer visibly exhibited increased viscosity and a reduction in the thickness of the melt layer was observed. This work would be the first time that the additive-particle effects on the melt layer were emphasized.

While characterizing binders for the BDP model, Cohen et al. [23] investigated the use of catalysts in an HTPB binder. It was found that the catalysts *n*-butylferrocene and polycarbonanesiloxane only affected decomposition when oxidizer was present in the binder, which led to the conclusion that catalytic reactions only affect AP processes or gas-phase reactions between the HTPB and AP. During this study, all samples contained carbon powder, which is believed to act as a radiation heat sink at the propellant surface, preventing any preheating of the binder.

King [19] at Atlantic Research Corporation had been working on various analytical models throughout the 1970s and toward the end of the decade published data on monomodal distribution propellants of AP-HTPB. King used a low solids loading, 73%, which was known to yield anomalous burning; however, the propellant burned normally. Close attention to King's formulas reveal that carbon black was used as an additive. Although it was not discussed within the work, this was most likely the embodiment of Handley and Strahle's [34] observations of particle additives affecting the melt layer, although other factors may have arguably contributed to the result, such as the radiation absorption of carbon additives.

In addition to their contribution to oxidizer distributions, Fong and Hamshere [26] studied two catalysts in HTPB-AP propellants: copper chromite and copper phthalocyanine. Both of these additives were seen to enhance plateau burning, and copper chromite even proved to create plateau burning in formulas that originally had none.

In the work from Frederick et al. [12], it was highly possible that the inclusion of the additive Ag white as 2% of the propellant was responsible for the absence of an extinguishment event, as seen earlier in similar formulas by Schmidt and Poynter [10], even though no discussion of this was included.

The 1990s saw a large amount of work focusing on additives in anomalous burning, and the first major study was conducted by Yin et al. [35], who looked at the use of the additive calcium carbonate ($CaCO_3$). The study focused on AP-PU sandwiches with the additive pressed into the AP pellets. The additive was able to produce anomalous burning in normal burning propellants, but what was of particular interest was that major inflection points on the burning rate curves corresponded to the onset of AP self-deflegration. Yin et al. carried out a study of AP-$CaCO_3$ chemical kinetics with the use of x-ray photoelectron spectroscopy to view the residual species on the extinguished surfaces. This reaction was found to create $CaCl_2$, which was believed to suppress the AP burning and explain the deflection point at the onset of AP self-deflagration; at lower pressures, it was speculated that the additive aided in AP melting, which increased the burning rate. A sandwich was produced with the additive in the binder and resulted in normal burning; however, this was not fully addressed in the discussion.

In Cohen and Hightower's [14] discussion of anomalous burning, the effect of solid additives on the binder melt layer was recognized for the first time. When comparing King's [19] formulas, the carbon black was identified as a viscosity-altering parameter, and the example of the automotive industry's practice of using graphite to increase the viscosity of motor oil was used as illustrative confirmation. This validated Handley and Strahle's [34] earlier observations concerning additives affecting binder flow. The theory proposed by Cohen and Hightower [14] stated that melt-layer viscosity contributes to the determination of the plateau onset, meaning that additives could potentially be used to control the lower pressure level of plateaus.

In the work by Klager and Zimmerman [20], the use of various binder additives such as amines, quaternary ammonium salts, and ammonium sulphate are presented as typical methods of producing anomalous burning in composite propellants. Negative-exponent propellants were revealed to be producible with the use of fusible salts that moderate combustion by producing copious amounts of ammonium ions that suppress AP dissociation and by "producing a greater thermal barrier" [20]. The negative-exponent formulas supplied used up to 84% AP, up to 19% Al, 15% PU binder, and 1% additive.

Oyumi et al. [36] from the Japan Defense Agency and from the Explosion Division of the Oita plant of Japan studied plateau burning with energetic binders: namely, BAMO/NMMO [3,3-bis(azidomethyl)oxetaine/3-nitratomethyl-3-methyloxetane]. The oxidizer, AP at 80% mass loading, was arranged in a trimodal distribution consisting of a 50/25/25 division with the sizes 200, 35, and 5 μm, respectively. Two varieties of iron oxide were tested, and although both produced mesa burning, Fe_2O_3 was found to create a higher average burning rate than Fe_3O_4. The mechanism given in this study championed the condensed-phase chemistry of the additives as the main burning mechanism, it was concluded that the melt layer had not affected the plateau. This was deduced from a microscale motor test that produced a near-identical burning rate at a single pressure to the value that was measured during strand testing.

During the mid-1990s, a series of patents was filed by Taylor [37] and Taylor and Hinshaw [38] from Thiokol Corporation on aspects of plateau-burning propellants. The main application discussed was the use of plateau propellants to create multiphase rocket motors, or motors that can have more than one specified thrust pattern during operation without the use of multiple grains or excessive mechanical augmentation to the motor hardware. The focus of these patents was the use of refractory oxides to produce both low- and high-pressure plateaus. The oxides reported were TiO_2, ZrO_2, Al_2O_3, SnO_2, and SiO_2 and were recommended at levels between 0.3 and 5%. These oxides in the size range below 0.02 μm were claimed to aid in the formation of the upper pressure-range plateau, whereas the size range above 0.4 μm was described to aid in the formation of the lower pressure-range plateau.

The exact locations and burning rates of the plateaus were shown to be determined by binder composition, mainly IPDI or DDI-cured HTPB, and the solid particle loading and sizes. One oxidizer distribution detailed consisted of a 400/1.7 μm bimodal distribution with a 1.63 coarse-to-fine ratio, which falls within Fong and Smith's [25] criteria of having a 60:40 or higher ratio. Within the reported claims of the patents, Taylor [37] and Taylor and Hinshaw [38] disclosed a broad scope of reported smokeless biplateau propellants consisting of AP loadings between 65 and 90% and elsewhere disclosed aluminized biplateau propellants with up to 20% Al (80–120 μm), although the plateaus plotted for the aluminized propellants were visibly less defined. A main importance is placed not only on the refractory oxide additive, but also on the curing additive, stating that DDI was the only curative capable of producing a biplateau burning curve in an aluminized propellant.

A brief thermogravimetric analysis (TGA) discussion shows that IPDI-cured HTPB vaporized quicker than DDI-cured HTPB and that the plasticizer is the first portion of the binder to vaporize. An experiment on binder gumstocks using laser pyrolysis showed evidence of an effect produced by the presence of TiO_2 in the binder and also a distinction in the effect by the size of the TiO_2; the effects described were the physical appearance of the scorched areas. Even though formulas of propellants that exhibit biplateau burning were highly defined within these patents, very little discussion of a mechanism or cause was mentioned; however, the curative and additive were described to be of high importance.

Brill and Budenz [39] from the University of Delaware published a study on the catalytic behavior of TiO_2 in light of the recent interest in it as an additive to produce plateau-burning-rate curves. Using flash pyrolysis, they showed that TiO_2 under 0.41 MPa (4.0 atm) pressure acted as a valid catalyst by not affecting the time to exotherm, but rather by accelerating the rate of gaseous product evolution. These experiments helped unravel the refractory oxides patented by Taylor [37] and Taylor and Hinshaw [38] by showing that not only does a viscosity mechanism exist, but more so by proving that a catalytic event exists. This was in contrast to work being done at the same time by Hinshaw and Cohen [40], who observed that TiO_2 only had a viscosity effect on propellant burning and was believed to be otherwise chemically inert.

In 2002, Ide [41] from the Australian Defence Science & Technology Organisation composed a report discussing the mechanisms of anomalous burning focusing on biplateau propellants. Here, Ide compiled an extensive review of the plateau mechanism and discussed the use of TiO_2 as an additive for producing biplateau propellants. The plateau mechanism was defined based on the review, and Ide summarized that biplateau burning could be achieved only by the use of DDI as a curative, a wide AP particle distribution containing fines on the order of 5 μm, coarse sizes larger than 150 μm, and a burning rate modifier such as TiO_2. Various aspects for tailoring the relative magnitude of the plateau were also discussed.

Price et al. [27] also conducted extensive testing on additive effects in anomalous-burning propellants [42,43]. Noting an interesting observation, Price et al. proposed that because fine AP does not thicken the binder melt layer, as Cohen and Hightower [14] suggested that fine powders should do, TiO_2 does not have a large effect on melt-layer viscosity, but rather alters the burning rate and controls anomalous burning through catalytic means. Cinematography of burning surfaces revealed that formulas with 0.02-μm TiO_2 had much stronger and solid flames than those observed on a baseline formula containing no additive. TGA analysis revealed that gasification was only accelerated by the TiO_2 when both the oxidizer and binder were present and that no catalytic effect was seen when each ingredient was tested individually with TiO_2. An investigation of extinguished surfaces did, however, show that baseline propellants had smooth surfaces and propellants containing TiO_2 were "littered with debris" [42], which was interpreted to be proof of near-surface catalytic reactions. Price et al. [27] also investigated Fe_2O_3 and found it to be a stronger catalyst than TiO_2, although the ability to produce or tailor plateau burning was less conclusive. Additional experimentation using hot-stage microscopy was conducted focusing on additives in the binder and alterations in the melting point [44]. Unfortunately, results were considered subjective and riddled with unforeseen variables, and so direct conclusions were difficult to make, although the results were very promising for quantifying aspects of additive use in anomalous burning.

Solid additives in composite propellants have been shown to have two main contributions to anomalous-burning rates. The first of these is by altering the viscosity of the binder melt layer, which in turn affects the suppression of oxidizer burning. Many of these additives have also demonstrated catalytic effects on the oxidizer, which accelerates the rate of gasification of the oxidizer. Additives used throughout the years include such chemicals as copper chromite, ferric oxide, carbon powder, ferrocene, iron blue, calcium carbonate, organics such as quaternary ammonia salts, various refractory oxides, and several more. Because of the endless varieties of additives that can be tested and the variations in their individual attributes and effects on the propellant combustion, this area has become a major focus of anomalous propellant research.

D. Summary

Over the past 50 years, a great deal of research and data have been accumulated on the subject of anomalous-burning behaviors. For the first time herein, an historical account has been made following the progression of these works with regard to the binder melt layer, oxidizer particles, and additives. With the initial prospects made by Steinz et al. [1], a burst of research took place around 1970. This initial work was then followed by a steady stream of continuing investigation that produced major breakthroughs periodically until the present day.

It is from this look into the past that the path into the future can be best seen. From lessons learned and improvements to old techniques, research can continue to progress and make new advancements in understanding the anomalous-burning phenomenon. Binder melt-layer data still need quantitative measurement methods, oxidizer behavior needs better understanding, and additives need to be fully characterized to understand their influences in propellant burning. By expanding this field, improved models can ultimately be created, enabling tailoring of these nonlinear burning rates. Multiple groups are still actively perusing the development of this understanding, including the authors of this paper, as well as others such as Fitzgerald and Brewster [45], who recently published work on oxidizer flame structure that will aid in fully comprehending the anomalous-burning mechanism.

III. Experiment

The experimental section of the present work focused on the use of nanoscale TiO_2-based additives in solid composite propellants. As shown previously by some groups and summarized earlier, this solid additive can have noticeable effects on anomalous burning [37,38,40–43]. Previous work conducted by the authors has also shown that nanoscale TiO_2 is an effective burning rate modifier [46]. However, very little has been published on details of the TiO_2 additives in previous work, and so the present study was conducted in the interest of exploring different varieties of TiO_2 and observing their alterations on a baseline propellant formulation that exhibits anomalous burning.

The propellant formula consisted of 70–80% AP as the oxidizer, 0–1% TiO_2-based additive, and an IPDI-cured HTPB binder that contained Tepanol (HX-878) as a bonding agent. The formulas for all propellants tested are listed in Table 1. The oxidizer was sized using imaging software on digital photographs of individual particles using an optical microscope and stage micrometer; additional details have been discussed elsewhere [46]. The average particle size, on the order of 200 μm per the manufacturer, was determined to be 223 μm, with a standard deviation of 55 μm. A histogram of the distribution is shown in Fig. 6.

The nanoscale TiO_2 was varied by two parameters: crystal structure and the element used to dope the additive. Pure TiO_2 was studied in three different crystalline structures (amorphous, anatase, and rutile), and in the anatase crystal phase, three different doped versions (aluminum, gadolinium, and iron) of TiO_2 were chosen for testing. The specifics of the additive for each formula are included in Table 1. The additives were all created by using a chemical synthesis method known as the sol-gel process. The crystal phases were achieved by heating the additive to the necessary temperature to facilitate the correct phase change before use; the structures were confirmed using x-ray diffraction (XRD). Exceptions to this were

Table 1 Formulas used to test TiO_2 on plateau burning with binder composition of 90.3% HTPB, 8.7% IPDI, and 1.0% Tepanol

Formula	AP %	%	TiO_2 crystal phase	Dopant %: element
		Baselines		
*B*1	70	——	——	——
*B*2	80	——	——	——
		Crystal Phases		
*C*1	70	0.5	Amorphous	——
*C*2	70	0.5	Anatase	——
*C*3	70	0.5	Rutile	——
*C*4	80	0.5	Amorphous	——
*C*5	70	0.5	Anatase [a]	——
*C*6	80	0.5	Anatase [a]	——
*C*7	80	0.5	Rutile	——
		Doped Additives		
*D*1	70	1.0	Anatase [a]	3—Al
*D*2	70	1.0	Anatase [a]	5—Al
*D*3	80	0.5	Anatase [a]	3—Al
*D*4	80	0.5	Anatase [a]	3—Fe
*D*5	80	0.5	Anatase [a]	3—Gd

[a] Modified sol-gel synthesis method.

formulas *C*5 and *C*6 and the complete doped series, which used a modified sol-gel technique that was able to directly produce anatase-phase TiO_2 without additional heating, again confirmed by XRD analysis. Particle sizes of the additives were determined by transmission electron microscope (TEM) images of the particles. The amorphous and anatase particles were 10–15 nm in diameter, and the rutile particles were 50 nm in diameter. A TEM image of anatase TiO_2 can be seen in Fig. 7.

The propellant was mixed and tested in the authors' laboratory. Twenty-gram batches of propellant were created by using a hand-mixing method in beakers. The propellant was held in a vacuum for long durations during production to aid in evacuation of air pockets and the release of ammonia during Tepanol's bonding process. Validity of the mixing method has been demonstrated previously by comparing separate batches with those produced by a mechanical mixing method simulating large-scale industrial production [47]. Samples were cast into 0.25-in.-diam (6.35-mm-diam) Teflon tubes and were cured at 55°C for one week.

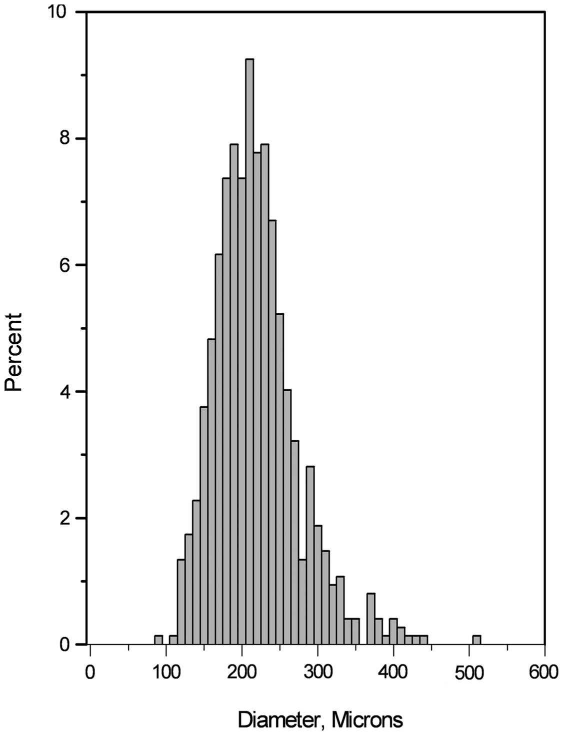

Fig. 6 Average particle size of AP showing a normal distribution around 223 μm.

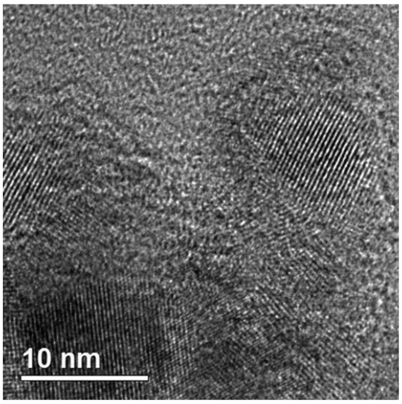

Fig. 7 TEM image of anatase TiO_2 showing the average particle diameter as 10–15 nm.

Burning rate testing was conducted using a high-pressure strand bomb, based on the Crawford strand burner concept, capable of testing up to 34.47 MPa; for this study, tests were conducted between 3.45 and 17.24 MPa (34.0–170.1 atm). The samples were cut into 1-in.-long (25.4-mm-long) strands and inhibited along the walls to ensure proper end burning. Ignition was achieved by the use of a nichrome wire pressed gently against the ignition surface. The strand burner was equipped with pressure transducers and a broadband visible photodiode (Si) by New Focus. The burn times were determined by the inflection points in the chamber pressure signal and were validated with the photodiode's time history of the flame's visible emission. The pressure rise within the chamber was observed to never exceed 10% of the initial pressure; the recorded burning rate measurement for each test corresponds to the average pressure seen during the burn. Further details of the burning facility and practices were documented by Carro et al. [48].

IV. Results

The first formulas produced and tested were the baseline series that were recently used in another study exploring nano additives [46]. Figure 8 shows baseline formula *B*1 (containing 70% AP) and baseline formula *B*2 (containing 80% AP) plotted by data points representing individual tests, with overlaid piecewise curve fits; all propellant formulas were displayed in this fashion. As expected, the higher AP loading level produced higher burning rates than the lower loading at respective pressures. A plateau was apparent in formula *B*1 starting at about 6.21 MPa (61.2 atm) and extending to the 17.24 MPa (170.1-atm) region and had a slightly negative pressure exponent. Formula *B*2 does not have a distinct plateau but did have a shift in

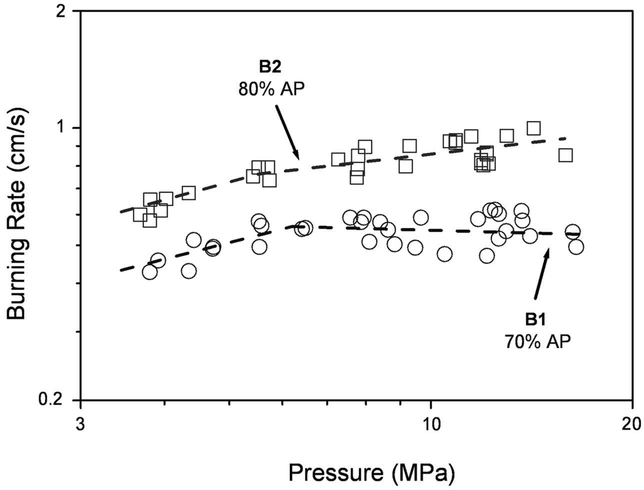

Fig. 8 Burning rate plot of baseline formulas; *B*1 containing 70% AP and *B*2 containing 80% AP. The binder used in all formulas consisted of 90.3% HTPB, 8.7% IPDI, and 1.0% Tepanol. Data taken from authors' previous work [46].

exponent value again near 6.21 MPa (61.2 atm), where the pressure exponent decreased slightly with pressure. The data points shown for both baselines represent propellants from multiple mixture batches to demonstrate repeatability.

The results from the three TiO_2 crystal structures (Table 1, *C*1–*C*3) are compared in Fig. 9. Each of these three formulas used the low AP loading percentage of 70% and contained 0.5% additive. As can be seen, all of the individual test points for the three crystal structures fall within the same scatter area, and so all three formulas are represented in Fig. 9 by a single curve. By comparing this average result with the curve of the 70% AP baseline formula *B*1, it is evident that the TiO_2 additive succeeded in increasing the burning rate by a marginal degree and also showed a slight drop at the higher-pressure region to a slightly negative pressure exponent, creating a mesa event. In contrast to the plateau burning, formula *C*4 (containing 80% AP and 0.5% amorphous TiO_2) showed a strong linear curve extending smoothly throughout the full pressure region tested (Fig. 10). When compared with *C*4's respective 80% AP baseline *B*2, the slope of *C*4 was seen to nearly match the initial pressure exponent of *B*2 at pressures below 6.21 MPa (61.2 atm), but clearly diverged to larger burning rates at pressures above 6.21 MPa.

The modified sol-gel method was used to produce additives for two formulas that tested anatase TiO_2 at both 70 and 80% AP (*C*5 and *C*6), shown in Fig. 11. For these two additives, the propellants produced linear burning rate curves over the entire pressure range; this trend is in strong contrast to their respective baselines shown in the burning rate plot by dashed lines. A comparison between the two formulas shown in Fig. 11 and their respective baselines indicates that *C*5 (with 70% AP) produced a larger overall burning rate increase over its respective baseline *B*1, even though in a direct comparison between the two, *C*6 (with 80% AP) exhibits a larger overall burning rate, as would be expected by the higher AP content. Formula *C*7 (with 80% AP and 0.5% rutile TiO_2) can be seen in Fig. 12 and reveals a linear burning rate curve that was within very close proximity of its respective baseline *B*2.

The doped study was conducted by using three separate elements to dope the TiO_2 additive: Al, Fe, and Gd (*D*1–*D*5, Table 1). All of the additives for the doped-TiO_2 study were synthesized using the modified sol-gel technique. The first plot in Fig. 13 shows two formulas that both have Al-doped TiO_2 but at different levels; *D*1 has 3% Al content within the TiO_2, and *D*2 has 5% Al content. In this plot, the two Al-doped formulas are seen displayed against their respective 70% AP baseline *B*1 and also against the burning rate curve fit from the other TiO_2 formulas that produced an anomalous-burning rate feature: formulas *C*1, *C*2, and *C*3. It can be seen that formulas *D*1 and *D*2 both created a defined mesa burning rate between the other two curves shown and dropped below the baseline

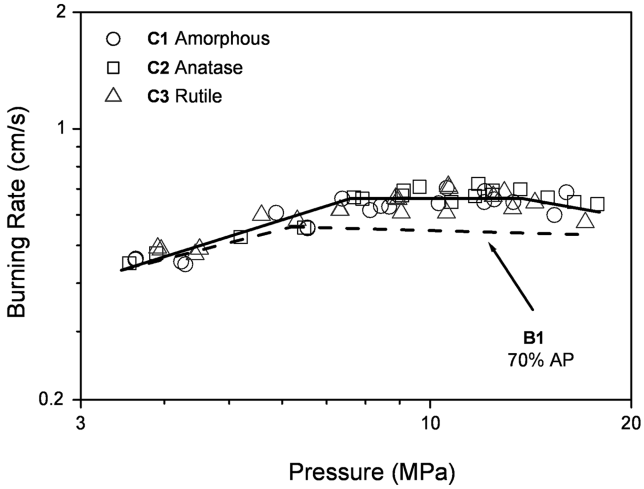

Fig. 9 Burning rate plot of propellants containing 70% AP and 0.5% TiO_2 but differing in crystal structure; *C*1 was amorphous (10–15 nm), *C*2 was anatase (10–15 nm), and *C*3 was rutile (50 nm). Baseline *B*1 is also shown as a reference.

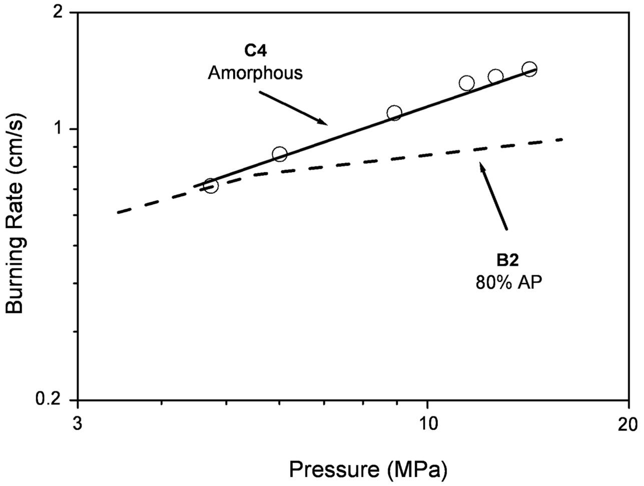

Fig. 10 Burning rate plot of the *C*4 formula which contained 80% AP and 0.5% amorphous TiO_2 (10–15 nm). Baseline *B*2 is shown as a reference.

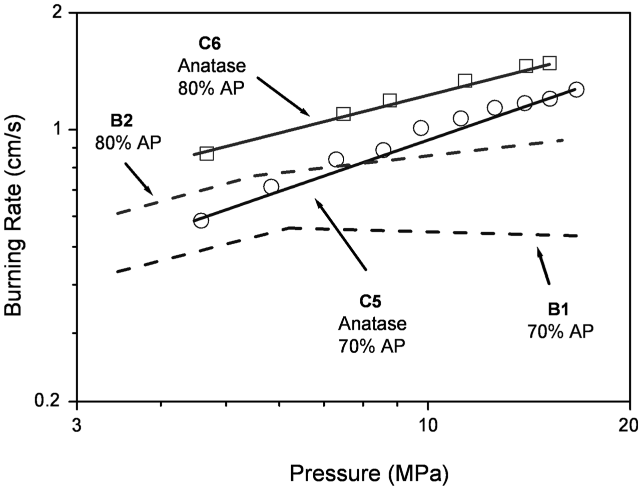

Fig. 11 Burning rate plot of propellants containing 0.5% anatase TiO_2 but with different oxidizer loading levels. *C*5 contained 70% AP and is plotted against its respective baseline *B*1, *C*6 contained 80% AP and is plotted against its respective baseline *B*2. This anatase TiO_2 was created with the modified sol-gel technique.

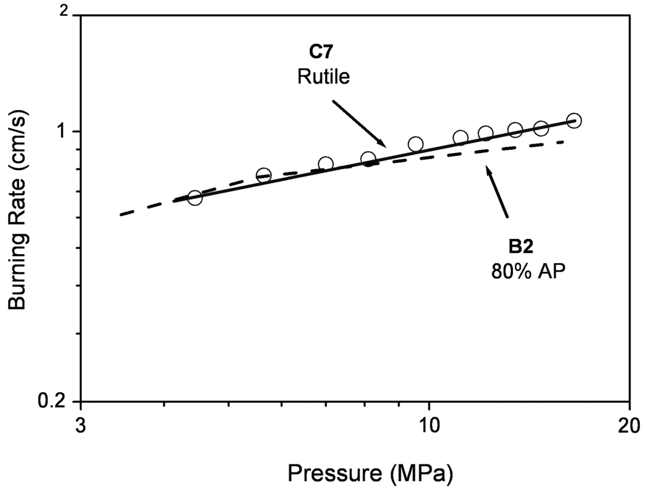

Fig. 12 Burning rate plot of formula *C*7 which contained 0.5% rutile TiO_2 and 80% AP, also shown is the respective 80% AP baseline, *B*2.

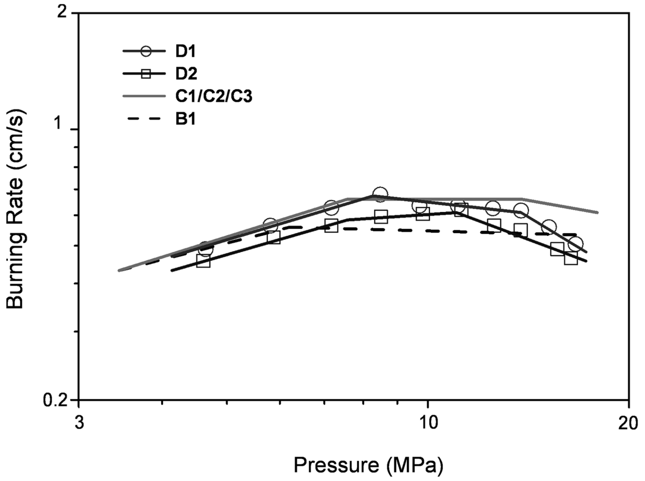

Fig. 13 Burning rate plot of aluminum-doped TiO_2 additives; *D*1 containing 3% and *D*2 containing 5% Al content within the TiO_2 nanoparticles which were added at 1.0%. For comparison, the 70% AP baseline, *B*1, and the curve fit for formulas *C*1/*C*2/*C*3 are also shown.

at high pressures. The increased Al-doping level *D*2 showed slightly lower burning rate magnitudes.

The type of element used to dope the TiO_2 was varied in the last set of formulas shown in Fig. 14, which all used 80% AP, 0.5% additive, and 3% doping; the respective 80% baseline *B*2 is also plotted. Formula *D*3 contained Al-doped TiO_2 and is seen to follow very near to the curve of *B*2, which was also closely followed by formula *C*7, as shown previously (Fig. 12). Unlike formula *C*7, the burning rate of formula *D*3 suddenly jumps near 13.79 MPa (136.1 atm) up to the burning rate values similar to other doped TiO_2 propellants at that pressure. The burning rate data from the other propellants (formula *D*4, which contained Fe-doped TiO_2, and formula *D*5, which contained Gd-Doped TiO_2) can be seen in Fig. 14 to lie in the same area of scatter and so were represented by a single curve fit.

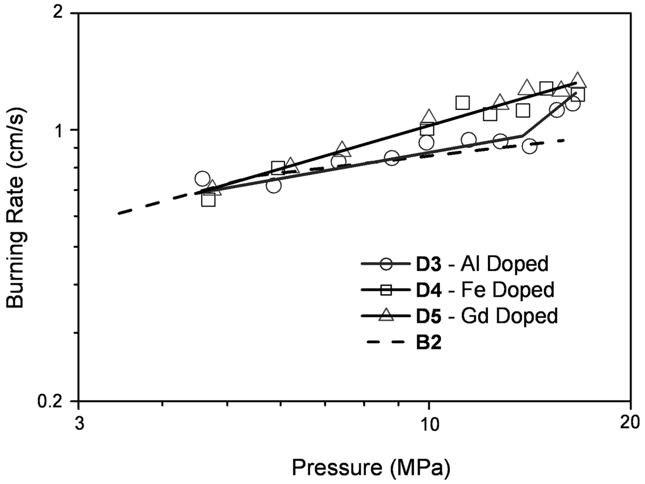

Fig. 14 Burning rate plot of propellants containing 0.5% TiO_2 doped with 3% Al (*D*3), 3% Gd (*D*5), and 3% Gd (*D*5). Also plotted for comparison is the burning curve for the 80% AP baseline, *B*2.

V. Discussion

An explanation for the anomalous behavior of the baseline propellant *B*1 rests strongly on the low percentage of solids. Between the two baseline formulas was an oxidizer loading increase of 10% of the propellant's total mass, and this increase in loading showed a drastic influence on the burning rates seen in Fig. 8. This dependence on oxidizer loading corresponds well with Steinz et al.'s [1] original observation, wherein a decreased solid loading increases the chances of anomalous burning, and the recurring proof in following studies [1,15,17]. The burning rates shown here for 70% AP are in stark contrast to King's [19] burning rate for 73% AP of the same size distribution. However, recall that King used a small addition of carbon powder in the propellants; this emphasizes the importance of all additives to their scope of influence on propellant combustion.

In both baselines, a transition point was seen at 6.21 MPa (61.2 atm), where the pressure exponent decreases. There are two possible explanations for this change in combustion response; it could be a result of the melt-layer viscosity and surface structure or a result of AP combustion, because that pressure roughly aligns with and resembles regime II burning of AP as described by Boggs [21]. However, because there was no major event at 13.79 MPa (136.1 atm), where regime III begins, it was doubtful that the AP self-deflagration was a key factor. This pressure region does correspond to where the oxidizer regression surpasses binder regression in AP-PBAN propellants, as was shown in sandwich studies by Price et al. [27] and which indicates that the surface structure and binder melt layer was more likely the responsible mechanism.

Other work by Price et al. [27] has focused on this same propellant formula, referred to as a coarse AP matrix. In one case, during testing to determine burnable limits, it was shown that this baseline formula successfully burned from atmospheric pressure up to 13.79 MPa (136.1 atm) [28]. The burning rates were recorded, and the resulting burning curve showed a plateau feature at the same pressure range but at a slightly lower burning rate magnitude [28]. This result was most likely due to a slight difference in the exact AP particle size distribution, and none was supplied in Chakravarthy et al.'s [28] publication.

By altering the crystal structure of the TiO_2 additive, no difference was observed in the overall burning rate curve (Fig. 9). Using the premise that the change in the burning rate versus the baseline *B*1 was a product of increasing the viscosity of the melt layer, then it can be stated that nanoparticles between 10–50 nm create the same degree of viscosity alteration. On the other hand, if this change in burning rate was a product of catalytic chemistry, then it can be stated that the crystal phase does not have an effect on the kinetics. At this point, the data do not favor one explanation over the other.

The behavior of formula *C*4, seen in Fig. 10, indicates that the additive has the ability to fully outweigh the anomalous-burning mechanism and return the propellant to normal burning behavior. The fact that *C*4 appears to be an extension of the initial burning curve of *B*2 in the lower pressure region indicates that the propellant simply burns normally and was not enhanced, therefore showing implications that these additives are affecting the melt layer and not chemical kinetics. The influence of the additive on the melt layer that produces the return to normal burning could be an increase in viscosity, as proposed by Cohen and Hightower [14]. This result then indicates that formulas *C*1, *C*2, and *C*3 were acting as inert particles and simply affecting the viscosity, which is in disagreement with Brill and Budenz's [39] conclusion about anatase TiO_2 [39].

Anatase TiO_2 was also produced by the modified sol-gel method, and the first two of these formulas, *C*5 and *C*6, clearly showed drastically increased burning rates, thus indicating a catalytic enhancement of the burning rate (Fig. 11). Note that in Fig. 9 for the same amount of TiO_2 additive and AP oxidizer (the only difference being the way the TiO_2 was manufactured), no significant alteration of the propellant burning rate was observed relative to the baseline. These seemingly contradictory results are now in agreement with Brill and Budenz [39] and show that certain characteristics of the TiO_2 particles, dependent upon synthesis technique alone, may play a vital role in the catalytic effectiveness of the additives on propellant burning. This result may also shed light on why there have been so many disagreements over the years on TiO_2's exact effect on propellants.

Rutile TiO_2 (manufactured using the sol-gel technique) was shown in formula *C*7 to have very little effect on the burning rate at high solids loading (Fig. 12) and again points to a physical mechanism related to binder flow. This effect is in contrast to the anatase TiO_2 results in Fig. 11 and shows that the anatase crystal structure has catalytic abilities not present in the other structures that may also be greatly influenced by synthesis technique. In earlier work by the authors, differential scanning calorimetry and TGA analysis of additives synthesized by the original sol-gel method confirmed this conclusion [49]. Although in that work, the burning rates were interpreted to indicate that anatase was the only additive capable of creating a plateau-burning propellant, but the subsequent tests and analyses included in this work have proven that it is not always the case.

Formulas *D*1 and *D*2 explored varying of the dopant levels of Al in the TiO_2 (Fig. 13); the result of a strong mesa geometry unlike any burning curves seen to this point indicated that doping certainly affects the additive's performance. Brill and Budenz [39] suggested that TiO_2 showed a reduction in the AP redox chemistry and that this could lead to reduced burning rates [39]. If the doping enhances this redox reduction, then it could explain the mesa burning.

Other doping elements were explored in formulas *D*4 (Fe) and *D*5 (Gd); when these are contrasted to Al-doping in formula *D*3 at 80% AP in Fig. 14, it is seen that they did not have the same effect as Al. Both *D*4 and *D*5 behaved similarly to *C*4, which was reasoned to indicate a higher emphasis on viscous effects than on a catalytic mechanism. *D*3, on the other hand, maintained burning rates similar to the baseline until higher pressures, when the burning rate begins to increase. This transition might indicate that Al-doping is unique unto itself, creating a burning rate curve not achieved with any other additive. Doping can definitely be seen here as yet a further parameter that can be used to adjust propellant burning rate without the need to replace large amounts of oxidizer or binder and without complicating propellant production.

These interpretations of the burning rate behaviors are well suited to provoking thought on what possible mechanisms are underlying the observations but should not be taken as conclusive until they can be supported with more quantitative details obtained in experiments with more controlled variables than are possible in the current work. This point emphasizes the ongoing trend discussed previously in the literature review that shows a need for better understanding of the kinetics and other phenomena that take place on or near the burning surface and that can only be achieved by improving the experimental techniques.

VI. Conclusions

Presented within the present paper was a comprehensive review of the literature that has contributed to the understanding of anomalous burning. The paper outlined the historical evolution of the mechanism relating the binder melt layer to its viscosity and the propellant's surface structure during burning. An extensive amount of recent work has focused on the use of metallic oxides and inspired the current work that investigated TiO_2-based additives and emphasized how different alterations of the binder could affect propellant burning.

The baseline formulas without additives were shown to exhibit abnormal-burning curves even though they consisted of a monomodal oxidizer and used IPDI-cured HTPB binders, which are usually not used in plateau propellants; however, the low solids loading was able to produce enough burning suppression to cause plateau and other behavior. The nanoscale TiO_2, even at the lowest suggested level within the literature [37,38], proved to have the ability to significantly alter the anomalous burning. Anatase was seen in the present work to be the leading candidate between the three crystalline structures for a catalytic additive, which agrees with Brill and Budenz's [39] work, although the synthesis method proved to be a major factor in the catalytic properties. The ongoing debate between whether TiO_2 affects burning by altering the binder flow's viscosity or interacts in the chemical kinetics was not discernible within the analysis of this work. However, doping the additive proved to be an effective method of further altering its influence on the propellant combustion. Among the doping elements investigated, Al proved to be of most interest. To the authors' knowledge, the present work contains the first burning rate results for composite propellants containing metal-doped TiO_2 nanoparticles manufactured using the sol-gel technique.

After digesting the extensive amount of information found in the literature review and understanding the implications of the current experiment, numerous routes for the next steps in experimentation can be considered. In regard to further propellant testing, varying curative, oxidizer distribution, and solids loading would all be potentially insightful parameters to alter. However, much of the analysis of the current work was restricted by the pressure range tested, and so future experiments should be conducted at wider pressure ranges to fully grasp burning rate behavior as a function of pressure.

Acknowledgments

This project was done under the support of the Missile Defense Agency's Missile Defense Science, Technology and Research (MSTAR) program, with Pashang Esfandiari as contract monitor (contract HQ0006-05-C-0023). In addition, the authors would also like to thank Alex LePage and Thomas Sammet for their assistance in testing some of the propellants studied within this project. This paper has been approved for public release per 08-MDA-3703 (28 July 2008).

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