TAILORING THE PLATEAU BURNING RATES OF COMPOSITE PROPELLANTS

BY THE USE OF NANOSCALE ADDITIVES

A Thesis

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ABSTRACT

Tailoring the Plateau Burning Rates of Composite Propellants
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Composite propellants are composed of a solid oxidizer that is mixed into a hydrocarbon binder that when polymerized results in a solid mass capable of self-sustained combustion after ignition. 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. It is not unusual for solid-particle additives to be added to propellants in order to enhance burning rate or other properties. However, the effect of nano-size solid additives in these propellants is not fully understood or agreed upon within the research community. The current project set out to explore what possible variables were creating this result and to explore new additives.

This thesis 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 TiO₂-based additives in AP-HTPB composite propellants was performed. The baseline propellant consisted of
either 70% or 80% monomodal AP (223 μm) and 30% or 20% binder composed of IPDI-cured HTPB with Tepanol. Propellants’ burning rates were tested using a strand bomb between 500 and 2500 psi (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.
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CHAPTER
INTRODUCTION

Solid propellants have been in existence for hundreds of years, originally in the form of black powder used to propel rudimentary rockets and to create colorful flames in firecrackers. In the 1940s composite propellants were developed and now function as a dominant form of solid propellants throughout the world serving functions such as gas generators for airbags and actuators, and as propulsion sources for small tactical missiles, large space-access rockets, and complicated control systems for attitude control. These composite propellants are comprised of a solid oxidizer particle (typically between 2 and 400 $\mu$m in size) mixed into a lengthy hydrocarbon binder that when polymerized produces a solid burnable rubber or plastic. By using less energetic chemicals than other forms of solid propellants, composite propellants have a profoundly high level of inertness; when manufacturing a full solid rocket motor the propellant is even cut with saws and tooled on mills with very little hazards. This exceptional level of safety, combined with the simplicity of solid rockets, their instant-readiness, and long shelf-lives, account for their global popularity.

Many of these benefits of a solid rocket motor have to do with not only the propellant state but also the hardware systems of the motor. A standard motor, as shown in Fig. 1, has four main components: a case, nozzle, grain, and igniter. The case is either a metallic or composite filament material pressure chamber that can be of any geometry,

This thesis follows the style of the *Journal of Propulsion and Power.*
typically cylindrical or spherical. The case has an opening that is fitted with the nozzle which facilitates in the directional control of the thrust as well as accelerating the supersonic exhaust thrust which chokes at the nozzle throat. The propellant is contained within the case and is usually formed into a specific geometry referred to as a grain; the shape of the grain dictates the internal pressure and therefore thrust of the motor by controlling the amount of propellant surface area exposed during the motor burn. The igniter is used to initiate the self-sustained burning of the propellant grain and can be located at various locations within the case.

Figure 1. Cross-sectional schematic illustrating the four main components of a solid rocket motor; the nozzle, case, grain, and igniter.

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. Traditional propellants follow a direct relationship between burning rate and pressure 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 (when plotted on a log-log graph) 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 non-linear 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 near-linear relationship with 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.
CHAPTER II
BACKGROUND

The direct study of anomalous 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: the 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 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 their work on burning-rate-tailoring additives could be put into perspective relative to established observations of anomalous burning.

Binder Melt Layer

One of the earliest groups to publish on the phenomenon of plateau burning within composite propellants was the work done by Summerfield at Princeton University in the late 1960s. While working on an early one-dimensional model for composite
propellant combustion known as the Granular Diffusion Flame Model, Summerfield and coworkers proposed several instrumental deductions on the cause of plateau burning as well as multiple significant observations.\textsuperscript{1} Plateau burning already existed and was widely seen in the propellant industry, as evident by an early NASA report on propellant selection,\textsuperscript{2} but lacked published evidence in the composite propellant field. One of the key statements proposed by Summerfield 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. 2, 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 the plateau region but elsewhere resemble typical burning characteristics. Burning curves are traditionally described by the following equation in which $r$ is the burning rate, $P$ is the chamber pressure, $a$ is an empirical coefficient based on grain temperature, and $n$ is known as the pressure exponent.\textsuperscript{3}

$$r = aP^n$$

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. Summerfield first decided that these three behaviors were created by the same mechanism which 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. Summerfield 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.

![Diagram of anomalous burning behaviors](image)

Figure 2. Typical behavior of the three types of anomalous burning: plateau, mesa, and intermittent extinction. Plateau burning is characterized by a pressure region in which the burning rate levels off. Mesa burning is characterized by a pressure region in which the burning rate becomes negative and can either recover to a positive slope again or result in an extinction point. Intermittent extinction burning is characterized by a pressure region in which the propellant can not sustain proper burning but exhibits normal burning at lower and higher pressures.

Summerfield and coworkers 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 general, the PU binder-based propellants tested by Summerfield et al. demonstrated mesas around 200-600 psi (20.4-40.8 atm) and extinguished at ranges of 600-1500 psi (40.8-102.1 atm). PBAA and PBAN binders showed a slight plateau effect at pressures under 100 psi (6.8 atm) or above 500 psi (34.0 atm); a few formulas extinguished at 500-600 psi (34.0-40.8 atm). Polysulfide (PS) binders exhibited plateaus in the 400-800 psi (27.2-54.4 atm) range, and one formula extinguished near 900 psi (61.2 atm). Summerfield also reported that sample size did not have a large affect on burning rates or curve shapes except for the smallest size tested, 0.125-in (3.2-mm) square.

Another group formed between Boggs, of the Naval Weapons Center at China Lake, together with Beckstead and Derr (at the time both at Lockheed Propulsion) presented scanning electron microscope (SEM) observations of extinguished burning surfaces of ammonium Perchlorate (AP)-based propellants.\textsuperscript{4,5} These studies focused mostly on AP-PU propellants but also explored, to a limited degree, carboxy-terminated polybutadiene (CPTB) binders and as oxidizers: potassium perchlorate (KP) and cyclotetramethylene tetranitramine (HMX). The PU binders studied only burned, at the most, up to 600 psi (40.8 atm), and some showed unsteady burning below 100 psi (6.8 atm). Here, Boggs et al. confirmed Summerfield’s 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.

Figure 3. Conceptual diagram of the binder melt layer in a basic composite propellant using a one-dimensional flame representation. In the left image, the melt layer is shown at near-level with the AP surface which results in normal burning. In the right image, the melt layer is higher than the AP particles resulting in a flow of the molten binder which partially covers one AP particle and the other, demonstrating the extreme, is completely submerged.

Notably in the PU-AP propellants, which were comprised of 26% binder and showed upper deflagration limits no matter what AP size was used (8, 50, and 200 \(\mu\)m), 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. 3, where 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 600 psi (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 which 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 Summerfield’s explanation and set forth the need to better understand the binder in the propellant structure.

Varney and Strahle, at Georgia Institute of Technology, conducted two-dimensional sandwich studies exploring a wide range of binders consisting of PU, PS, PBAA, and CTPB primarily by observing SEM images of extinguished surfaces. Sandwich tests investigate propellant combustion by structuring individual laminas of binder and fuel together creating a two-dimensional approximation of an actual propellant. Not only did this particular study have a diverse scope of binders, it also contained pressures up to 2400 psig (164.3 atm) as well as compared the behaviors observed with those of AP deflagration as described by Boggs and coworkers earlier. Observations proved that binder melt layers were being seen for all binders at all pressures, 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.
Up to this time, proprietary industry research had been contributing greatly to composite propellant development in various aspects. After the mid 1970s, the industry as well 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. of Aerojet Solid Propulsion Company released reports on gas generators that used negative pressure exponent slopes.\textsuperscript{7,8} These papers not only revealed the potential usefulness of anomalous-burning propellants but showed a strong industry involvement in the development of such applications. A propellant with an $n$ value of $-2.5$ was described as a “practical negative exponent propellant”\textsuperscript{7}. Later on, burning rate plots were given for AP-PU propellants with and without aluminum (Al), displaying strong mesas and plateaus at the 400-1000 psi (27.2-68.0 atm) range.

Contrary to the findings of Steinz et al.,\textsuperscript{1} sample size was proven to have a large effect on burning curves in the work of Cohen et al. For their project, multiple strand size tests and a corresponding motor test showed that the test scale had a large effect on the burning curve. Both strand sample sizes tested produced mesas at 300 psi (20.4 atm) and extinction limits near 500 psi (34.0 atm), while the motor recovered from the mesa at 300 psi (20.4 atm) in a shallow plateau, recovering to a positive exponent near 1000 psi (68.0 atm). This difference between strand tests and motor tests was most likely a result of a phenomenon known as erosive burning in which the geometry of the propellant grain and the convective flow within the motor chamber affect the propellant’s burning rate.
Schmidt and Poynter, also of Aerojet Solid Propulsion Company, in 1980 published work focusing on metal particle combustion, but revealed several important characteristics of propellant binders, notably concerning hydroxyl terminated polybutadiene (HTPB).\textsuperscript{9} Often times liquid additives are mixed into binders to help create improved propellant mechanical properties, particle-to-binder bonding, and to adjust curing characteristics.\textsuperscript{3,10} In this study, the effect of plasticizers and curatives was investigated and showed correlations to burning rates and suppressed burning. With increasing amount of dioctyl adipate (DOA) in the binder, the propellant was seen to have an ever-increasing extinction zone which culminated in making the propellant unburnable under 2000 psi (136.1 atm) when the binder was loaded with 35\% DOA. The plasticizer isodecyl pelargonate (IDP) was seen to have far less irregular burning trends when compared to the DOA. In an un-plasticized binder, isophorone diisocyanate (IPDI), dimeryl diisocyanate (DDI), and toluene diisocyanate (TDI) curatives were compared showing that they as well varied the suppression level of the burning, with TDI propellants burning the closest to expected results and DDI having the most severe extinction zones. 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 headed up by Osborn studied curative effects in burning rate and SEM imaging of extinguished surfaces.\textsuperscript{11} Again DDI and IPDI binders were compared in HTPB-AP propellants with bimodal (35:52, 400/20 \(\mu\text{m}\)) 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\textsuperscript{9} 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. Using the expressions formulated
by Xu et al.,\textsuperscript{12} Frederick et al.\textsuperscript{11} emphasized the need to quantitatively determine the AP
surface area covered by molten binder at various pressures; it was also stated that the
SEM images were not of high enough quality to definitively prove this hypothesis at the
time.

Norm Cohen (now of Cohen Professional Services) and Hightower at Thiokol
published a paper in which addressing and explaining plateau burning was the main
focus.\textsuperscript{13} In their report, an extensive review and comparison of Miller’s,\textsuperscript{14,15} Foster’s,\textsuperscript{16,17}
and King’s\textsuperscript{18} 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 also considered the surface structure geometry that had been reported by the SEM observations made by the multiple groups previously discussed. The main aspect in surface geometry was the relative location of the AP surface to the binder surface as first observed in SEM use by Derr and Boggs. If the AP particles extend above the binder, as was seen at low pressures, then the melt layer would not be expected to interfere with AP deflagration. On the other hand, if the surfaces are nearly even or if the AP particles are recessed, then the binder melt layer has a greater likelihood of flowing onto the AP surface. Cohen and Hightower asserted that these two mechanisms, melt layer thickness and surface structure, alone 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.

By coupling melt layer thickness and viscosity, the plateau phenomenon could be explained as starting when the viscosity reduced to a point where 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 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.” Over two decades after Summerfield’s original work, binder suppression of the oxidizer was still viewed as an unexplored phenomenon.

Klager and Zimmerman of GENCORP/Aerojet Solid Propulsion Company authored an extensive review on burning rate tailoring parameters that had several mentions of anomalous burning, most of which are discussed in the additive section below. In this work, anomalous propellants are described to inherently exhibit very low $\pi_k$ 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”. A majority of the data presented in this work depended on additives for anomalous burning and are further discussed in the additive review.

Even though it was not discussed within the work of Klager and Zimmerman, a connection also existed between anomalous burning and the liquid strand measurements described. It was explained that during propellant production a sample from each mixture batch was usually tested in a standard strand bomb prior to curing the entire batch and that the resulting burning curve highly resembled the burning curve of the fully cured propellant. This was illustrated with plotted examples of a PBAN-AP-Al propellant that displayed no anomalous burning in either the cured or uncured stages. Considering this, the importance of the melt layer thickness comes into question; this is
because in the uncured state, the entire propellant binder was a liquid from the start and yet for such a formula no anomalous burning was produced. Using this comparison in a propellant that exhibits anomalous burning could offer insight into the dependence of the thickness of the melt layer to its ability to over-flow the oxidizer.

All of these groups have contributed to the overall understanding and characterization of the melted layer of the binder in composite propellants. They have showed 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, also can 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.

Oxidizer Contributions

In Summerfield and coworker’s 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 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. 4; here it can be seen that AP will not sustain deflagration below 300 psi. 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.

![Figure 4. AP Deflagration rates divided into the four regimes as defined by Boggs, taken directly from source.](image)

The significance of these data to plateau burning continues to be a point of speculation. Region III, as described by Boggs, 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, Strahle and coworkers postulated
that the binder/oxidizer diffusion flame 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 also noted that extinguished AP showed evidence of a molten froth layer on the surface which 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.

![Figure 5. A conceptual description of the multiple flame (BDP) model first proposed by Beckstead, Derr, and Price.](image)

At the beginning of the 1970’s, Beckstead, Derr, and Price at Lockheed Propulsion published their famous model based on multiple flames, commonly referred to as the BDP 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 in which the products of the previous flames would mix and combust; this can be seen visually in Fig. 5. The conceptual illustration created earlier, Fig. 3, can be recreated with the adaptation of this new flame geometry and can be seen in Fig. 6. 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.

Figure 6. A conceptual schematic showing the binder melt layer illustrated with the BDP multiple flame model. The left image shows normal burning when the melt layer is at or below the AP particle surface. The right image shows a scenario where the AP surface is lower than the melt layer surface causing a flow which partially covers one AP particle, causing the flame structure to diminish in size, and completely extinguishes the other particle's flame.
Derr and Cohen, at Lockheed Propulsion, were one of the first groups that did a great deal of work to better catalogue the physical parameters of the various binders.\textsuperscript{23} 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 was conducting studies on additives that could inhibit AP combustion.\textsuperscript{24} 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. It is important to note that the mechanism created with Glaskova’s additives were a chemical kinetic mechanism as outlined in his work.

From Hercules Inc., Miller and Foster released several informative papers throughout the early 1980’s cataloguing 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.\textsuperscript{14,15} This work supplied valuable comparisons of monomodal formulas (6, 20, and 200 $\mu$m), 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).

Using an IPDI-cured HTPB binder, several anomalous behaviors were observed. Most notable was the intermittent extinction seen with the 6-μm AP at 77% loading and the 6/20-μ AP at 75% loading; both were burnable at 500 and 1500 psi (34.0 and 102.1 atm) but could not burn at 1000 psi (68.0 atm). Foster and coworkers supplemented this work with studies looking further at various oxidizer sizes and loadings, finding favorable conditions for anomalous burning, most notably above 1000 psi (68.0 atm) with very fine AP sizes in 75% AP.16,17

Wang and his group from Northwestern Polytechnical University in the People’s Republic of China developed a model based on the BDP structure which attempted to include the binder melt mechanism to accurately predict the various types of anomalous burning.12 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 released a paper focusing on wide-distribution AP formulas directly corresponding to their ability to produce plateau burning rate curves.25 Using a statistical method, the burning rate data from twenty-two 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 since Fong was involved in publishing work on such catalysts during this time period. The plateaus seen were in the 1000-2000 psi (68-136.1 atm) pressure region and showed no distinct mesas or extinction points.

Another crucial oxidizer-governing observation was made during this investigation; Fong noted that for a plateau to exist, the coarse-to-fine oxidizer ratio needed to be 60:40 or greater. Coarse was defined as particles 90-400 μm in size, and fine was defined as 20-55 μm in size. This finding may seem contrary to previous work which stated that increased fine AP resulted in a greater chance of anomalous burning, but recall that the 60:40 guideline proposed by Fong and coworkers was for plateau burning and not for mesa burning or intermittent extinction; and also that a metal catalyst was used.

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. The plateau burning propellants were explained by an enhanced primary flame between the fine AP and the binder melt layer containing the catalyst during low pressures when the burning rate was increased and at higher pressures where the burning rate was reduced, the binder melt was described to overwhelm the recessed AP and inhibit combustion, similar to earlier explanations.

At the same time during the mid 1980s, Price and his colleagues 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.\textsuperscript{28,29,30} 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 catalogued showing burning limits for various AP particle sizes from atmospheric pressure up to 2000 psi (136.1 atm). Price and coworkers also detailed how the melt flow interference correlates to the flame structure detailed in their 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, while IPDI-cured HTPB melted at 330-370 °C and PBAN melted at 480 °C.\textsuperscript{31}

Through SEM imaging of extinguished sandwich surfaces, Price et al. emphasize the importance of surface structure and describe it as the phenomenon called “disproportionation”.\textsuperscript{28} In this idea, the relative position of the AP surface and binder surface dictates the available O/F ratio, and if the surfaces are not at the correct level for the ideal O/F ratio, then they will correct themselves to continue normal burning. In the case of abnormal burning, the surfaces can not return to the ideal, relative levels, and thus combustion is hindered.

In 2007, Banerjee and Chakravarthy 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 435-1160 psi (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 which 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.

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, Strahle et al. studied four different catalysts: ferrocene, iron blue, ferric oxide, and copper chromite (Cu₂Cr₂O₅, identified here as the Harshaw Catalyst Cu 0202). Besides finding that the catalysts created a greater increase to the over-all burning rate when mixed into the pressed AP pellets and that iron blue and ferrocene led to the biggest 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 strongly discussed, which as expected can be highly influential in anomalous burning.

While characterizing binders for the BDP model, Derr and Cohen investigated the use of catalysts in an HTPB binder.23 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. Even though this was not expounded upon in the paper, both of these observations contribute to, or have an affect on, anomalous burning.

King at Atlantic Research Corp. had been working on various analytical models throughout the 1970’s and towards the end of the decade published data on monomodal distribution propellants of AP-HTPB.18 King used a low solids loading, 73%, which at that time was known to yield anomalous burning. However, King saw relatively normal burning at AP sizes of 5, 20, and 200 μm. Paying attention to the details of King’s formula reveals that these propellants contained “a trace of carbon black to opacify them”.18 Although it was not discussed within the work, this was most likely the embodiment of Handley and Strahle’s observations34 of particle additives affecting the melt layer, although arguably other factors may have contributed to the result such as the
radiation absorption of carbon additives. Cohen realized the importance of the additive and discussed it in relation to his viscosity hypothesis.\textsuperscript{13}

Besides their contribution to oxidizer distributions, Fong and Hamshere studied two catalysts in HTPB-AP propellants: copper chromite and copper phthalocyanine.\textsuperscript{26} Here the conclusion was that the burning rate was limited by binder thermal degradation at low pressure, below 1000 psi (68.0 atm), when catalyzed and limited by the gas diffusion process at higher pressures, above 1000 psi (68.0 atm). Both additives were seen to enhance plateau regions (extending their pressure range and increasing their burning rate) for DDI-cured HTPB propellants. For IPDI-cured HTPB formulas, which did not originally exhibit a plateau, copper chromite created a plateau in the 1000-2000 psi (68.0-136.1 atm) pressure range.

In the work by Frederick et al.,\textsuperscript{11} 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.\textsuperscript{9} No direct discussion was provided in the publication, however.

Another interesting study was conducted by Yin et al. who looked at the use of the additive calcium carbonate (CaCO\textsubscript{3}).\textsuperscript{35} The study focused on AP-PU sandwiches at pressures of 142-568 psi (9.7-38.7 atm). A majority of the work incorporated the additive into the pressed-AP pellet portions of the sandwiches, and no distinct size value was given for the additive except the description as superfine particles. Without the additive, the sandwich burning rates followed the typical linear curve on the log-scale plot, but the addition of the calcium carbonate saw the creation of a mesa burning curve
followed by a plateau. The interesting points of this curve were that data points below 284 psi (19.3 atm) matched up to Bogg’s AP deflagration curve (if it were extended forward), and at higher pressures, the burning rate levels off at a lower value. This indicates that the creation of the mesa and plateau was aligned with the onset of AP self-deflagration.

Yin et al. carried out a study of AP-CaCO₃ chemical kinetics with the use of X-ray Photoelectron Spectroscopy to view the residual species on the extinguished surfaces. The conclusion drawn was that the additive enhances AP melting at low pressures, increasing the burning rate, and that at higher pressures the AP was suppressed by the molten binder flow and by the production of CaCl₂. The production of CaCl₂ was found to be a product of reactions between the AP and CaCO₃ and was shown to retard the condensed-phase AP reactions. A sandwich was produced with the additive in the binder and resulted in normal burning. It was noted that the additive suppressed the binder melt layer, but no mechanism was credited.

In Cohen and Hightower’s discussion of anomalous burning,¹³ the effect of solid additives on the binder melt layer was recognized for the first time. When comparing King’s formulas,¹⁸ 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 Strahle’s earlier observations concerning additives affecting binder flow.³⁴ The theory proposed by Cohen and Hightower 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, 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. Quaternary ammonium salts are shown to suppress the burning rate and produce plateaus in the 400-2000 psi (27.2-136.1 atm) range for PU-AP-Al propellants. Other organic burning rate suppressants are shown to produce plateaus in the 500-1500 psi (34.0-102.1 atm) pressure range for the same family of propellants.

Negative pressure 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”. The negative exponent formulas supplied used up to 84% AP, up to 19% Al, 15% PU binder and 1% additive. A burning rate plot of such a propellant was given showing a mesa just above 1000 psi (68.0 atm) followed by a negative pressure exponent slope until about 1750 psi (119.0 atm) where the burning curve recovers to a positive slope extending beyond 2000 psi (136.1 atm). Surprisingly for this example, the burning curve did not change between strand tests and various-sized motor tests, which is not typical for most formulas as noted prior and shown in other plots within Klager and Zimmerman’s publication.

Oyumi from the Japan Defense Agency and his colleagues from the Explosion Division of Oita Plant of Japan studied plateau burning with energetic binders, namely
BAMO/NMMO (3,3-bis(azidomethyl)oxetaine/3-nitratomethyl-3-methylloxetane).\textsuperscript{36} 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 $\mu$m, respectively. Two varieties of iron oxide were tested, and Fe$_2$O$_3$ was seen to create a plateau over the pressure region tested, 1000-2200 psi (68.0-149.7 atm), when 1\% was added. When 3\% was added, the burning rate curve produced a mesa with the peak burning rate existing near 1600 psi (108.9 atm). The other variety of iron oxide studied, Fe$_3$O$_4$, was added at 3\% and created a mesa feature peaking at 1500 psi (102.1 atm) and lower than the burning rate magnitude achieved with Fe$_2$O$_3$. The focus here was on the condensed-phase chemistry of the additives, and it was concluded that the melt layer had not affected the plateau; this was deduced from a micro-scale motor test which 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 from Thiokol on aspects of plateau-burning propellants.\textsuperscript{37,38} The main application discussed was the use of plateau propellants to create multi-phase 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$_2$O$_3$, SnO$_2$, and SiO$_2$ and were recommended at levels between 0.3\% and 5\%. These oxides in the size range below 0.02 $\mu$m were claimed to aid in the formation of the upper pressure-range plateau, while the size range above 0.4 $\mu$m was described to aid in the formation of the lower pressure-range plateau.
Representative propellants described within the patents had low-pressure plateaus from typically between 200-700 psi (13.6-47.6 atm) and high-pressure plateaus from typically between 1500-3000 psi; the burning rate curves were recorded up to 7000 psi (476.3 atm) or higher. The exact locations and burning rates of these 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’s criteria of having a 60:40 or higher ratio.

Within the reported claims of the patents, Taylor discloses a broad scope of reported smokeless, bi-plateau propellants consisting of AP loadings between 65% to 90% and elsewhere discloses aluminized bi-plateau 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 bi-plateau burning curve.

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 TiO₂ in the binder and also a distinction in the effect by the size of the TiO₂; the effects described were the physical appearance of the scorched areas. Even though formulas of propellants that exhibit bi-plateau 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 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.\textsuperscript{39} Using flash pyrolysis, he showed that TiO$_2$ under 58.8 psi (4.0 atm) pressure acted as a valid catalyst by not affecting the time-to-exotherm but rather accelerating the rate of gaseous product evolution. These experiments helped unravel the refractory oxides patented by Taylor 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 who observed that TiO$_2$ only had a viscosity effect on propellant burning and was believed to be otherwise chemically inert.\textsuperscript{40}

In 2002, Ide from the Australian Defence Science & Technology Organisation composed a report discussing the mechanisms of anomalous burning and focusing on bi-plateau propellants.\textsuperscript{41} Here Ide compiles an extensive review of the plateau mechanism and discusses the use of TiO$_2$ as an additive for producing bi-plateau propellants. The plateau mechanism was defined based on the review, and Ide summarized that bi-plateau 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 are also discussed. Using an AP/HTPB propellant with 88% solids loading, a plateau was produced from roughly 150-1000 psi (10.2-68.0 atm), and another
plateau was produced at a higher magnitude roughly between 1500-2200 psi (102.1-149.7 atm).

Price’s group also conducted extensive testing on additive effects in anomalous-burning propellants.\textsuperscript{42,43} Noting an interesting observation, Price et al. proposed that since fine AP does not thicken the binder melt layer, as Cohen\textsuperscript{13} suggested that fine powders should do, TiO\textsubscript{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 $\mu$m TiO\textsubscript{2} had much stronger and solid flames than what was observed on a baseline formula containing no additive. TGA analysis revealed that gasification was only accelerated by the TiO\textsubscript{2} when both the oxidizer and binder were present, and that no catalytic effect was seen when each ingredient was tested individually with TiO\textsubscript{2}. An investigation of extinguished surfaces did however show that baseline propellants had smooth surfaces and propellants containing TiO\textsubscript{2} were “littered with debris”\textsuperscript{42} which was interpreted to be proof of near-surface catalytic reactions. Price’s group also investigated Fe\textsubscript{2}O\textsubscript{3} and found it to be a stronger catalyst than TiO\textsubscript{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.\textsuperscript{44} Unfortunately, results were considered subjective and riddled with unforeseen variables, 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.

Background Review

Over the past fifty 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 progress of these works with regards to the binder melt layer, oxidizer particles, and additives. To review the major milestones and contributions to this wealth of knowledge, a timeline has been assembled showing chronological progression within the subject, Fig. 7. As can be seen in Fig. 7, with the initial prospects made by Summerfield and coworkers, 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 that 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 non-linear
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 Brewster and Fitzgerald, who recently published work on oxidizer flame structure which will aid in fully comprehending the anomalous-burning mechanism.45
CHAPTER III
EXPERIMENT

The experimental section of the present work focused on the use of nanoscale TiO$_2$–based additives in solid composite propellants. The use of these additives in plateau burning has been proven highly effective. As shown previously by some groups and summarized above, this solid additive can have noticeable effects on anomalous burning.$^{37,38,40-43}$ Prior work conducted by the authors has as well 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 Teplanol (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 $\mu$m per the manufacturer, was determined to be 223 $\mu$m with a standard deviation of 55 $\mu$m. A histogram of the distribution is shown in Fig.8.
Table 1. Formulas utilized to test TiO$_2$ on plateau burning and organized within three subcategories: baselines, crystal phases, and doped additives.

<table>
<thead>
<tr>
<th>Formula</th>
<th>AP %</th>
<th>TiO$_2$ %</th>
<th>Crystal Phase</th>
<th>Dopant Element</th>
<th>%</th>
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<td>Baselines</td>
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<td></td>
<td></td>
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<tr>
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<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>B2</td>
<td>80</td>
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<td>-</td>
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<td>-</td>
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<td>-</td>
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<tr>
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<td>Anatase$^*$</td>
<td>Al</td>
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<tr>
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<tr>
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<td>Al</td>
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<td>Anatase$^*$</td>
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<td>Binder Composition</td>
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<td>90.3% HTPB</td>
<td>8.7% IPDI</td>
<td>1.0% Tepanol</td>
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* Indicates modified sol-gel synthesis method

Figure 8. Average particle size of AP showing a normal distribution around 223 $\mu$m.
By varying the oxidizer loading of the propellant between the two baseline compositions, a large temperature variable was introduced to the additive testing. This temperature difference was generated by the large shift in the equivalency ratio within the propellant. To achieve the stoichiometric oxidizer-to-fuel ratio for the ingredients used would require for the oxidizer (AP) to account for nearly 92% of the entire propellant mass. To quantifiably estimate the adiabatic flame temperature a thermochemical software program, PROPEP, was used to model the propellant. Working off user-defined variables and using elemental composition and heats of formation from a thermodynamic data library file, PROPEP was able to calculate many properties of the propellant including adiabatic flame temperature, specific impulse, and exhaust products. Figure 9 shows a plot of adiabatic flame temperature for selected oxidizer loading levels; this was used to determine the 880 K difference seen by the additive when used by the two different binder loadings.
Figure 9. Adiabatic flame temperature of selected oxidizer loading levels as calculated using PROPEP.

The nanoscale TiO₂ was varied by two parameters: crystal structure and the element used to dope the additive. Pure TiO₂ 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 TiO₂ 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). An exception to this was formulas C5, C6 and the complete doped series which used a modified sol-gel technique that was able to directly produce anatase-phase TiO₂ 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.10.

![TEM image of anatase TiO$_2$ showing the average particle diameter as 10-15 nm.](image)

Figure 10. TEM image of anatase TiO$_2$ showing the average particle diameter as 10-15 nm.

The propellant was mixed and tested in the author’s laboratory. Twenty-gram batches of propellant were created by using a hand-mixing method in open-ended 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 created during Tepanol’s bonding process. Validity of the mixing method has been demonstrated previously by comparing separate batches to those produced by a mechanical mixing method.
simulating large-scale industrial production.\textsuperscript{47} Samples were cast into 0.25-in (6.35-mm) diameter Teflon tubes and were cured at 55 °C for one week.

![Strand Bomb Schematic](image)

Figure 11. Strand bomb schematic showing sample mounting, ignition source, and instrumentation.

Burning rate testing was conducted using a high-pressure strand bomb capable of testing up to 5000 psi; for this study, tests were conducted between 500 and 2500 psi (34.0-170.1 atm). Argon was used as an inert fill gas during testing to ensure a controlled burning environment. Figure 11 shows a schematic of the strand bomb showing the sample mounting and instrument locations. The samples were cut into 1-in (25.4-mm) long strands and inhibited along the walls to ensure proper end burning. Ignition was achieved by running a high-amperage current through 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.
Figure 12. Typical plot of pressure and light emission data collected during a strand bomb test. The burning time is calculated by measuring the time length of the pressure rise inside the chamber and corresponding the data with the light trace’s indication of a flame (seen as an erratic, but strong, signal).

Burning rates were calculated by dividing the burning distance, which is simply the length of the sample measured prior to testing, by the burn time. The burn time was determined by the inflection points in the chamber pressure signal, this was then validated with the photodiode’s time history of the flame’s visible emission (Fig. 12). The pressure rise within the chamber was observed to never exceed ten percent 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.\textsuperscript{48} Data was then entered into plotting software that enabled curve fits of the burning rate over the complete pressure range that was tested; the completed plots are presented in the following section.
Several uncertainties are inherent in each test. To provide repeatability each formula was tested from separate batches to show mixing repeatability and multiple tests were conducted throughout the pressure range being studied. The error of the pressure transducer was supplied by the manufacturer as ±25 psi. The error of the burning rate could be found by conducting a propagation of error calculation for each individual burning rate. Separately, the error in propellant length was ±0.00056 in and the error in time was ±0.05 s (worst case interpolation). These errors are based on combing the interpolation error as well as the instrument error in the standard root-sum-square (RSS) method. A propagation of error calculation for a typical burning rate of 0.4 in/s was carried out and found to be only ±0.01 in/s, or 5%. 
Chapter IV

Results

The first formulas produced and tested were the baseline series which were recently used in another study exploring nano additives.\textsuperscript{46} Figure 13 shows baseline formula B1, containing 70\% AP, and baseline formula B2, containing 80\% AP, plotted by data points, representing individual tests, with overlaid piece-wise 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 B1 starting at 900 psi (61.2 atm) and extending to the 2500-psi (170.1-atm) region and has a slightly negative pressure exponent. Formula B2 does not have a distinct plateau but does have a shift in exponent value again near 900 psi (61.2 atm) where the pressure exponent decreases slightly with pressure. The data points shown for both baselines represent propellants from multiple mixture batches to demonstrate repeatability.
The results from the three TiO₂ crystal structures (Table 1, C1-C3) are compared in Fig. 14. 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. 14 by a single curve. By comparing this average result to the curve of the 70% AP baseline formula, B1, it is evident that the TiO₂ 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 C4, containing 80% AP and 0.5% amorphous TiO₂, showed a strong linear curve extending smoothly throughout the full pressure region tested, Fig. 15. When compared to C4’s respective 80% AP baseline, B2, the
slope of C4 was seen to nearly match the initial pressure exponent of B2 at pressures below 800 psi (54.4 atm) but clearly diverges to larger burning rates at pressures above 800 psi.

Figure 14. Burning rate plot of propellants containing 70% AP and 0.5% TiO$_2$ but differing in crystal structure; C1 was amorphous (10-15 nm), C2 was anatase (10-15 nm), and C3 was rutile (50 nm). Baseline B1 is also shown as a reference.
Figure 15. Burning rate plot of the C4 formula which contained 80% AP and 0.5% amorphous TiO₂ (10-15 nm). Baseline B2 is shown as a reference.

Figure 16. Burning rate plot of propellants containing 0.5% anatase TiO₂ but with different oxidizer loading levels. C5 contained 70% AP and is plotted against its respective baseline B1, C6 contained 80% AP and is plotted against its respective baseline B2. This anatase TiO₂ was created with the modified sol-gel technique.
The modified sol-gel method was used to produce additives for two formulas which tested anatase TiO$_2$ at both 70% AP and 80% AP (C5 and C6), here seen in Fig. 16. 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. 16 and their respective baselines indicates that C5, with 70% AP, produced a larger over-all burning rate increase over its respective baseline, B1, even though in a direct comparison between the two, C6, with 80% AP, exhibits a larger over-all burning rate as would be expected by the higher AP content. Formula C7, with 80% AP and
0.5% rutile TiO₂, can be seen in Fig. 17 and reveals a linear burning rate curve which was within very close proximity of its respective baseline, B2.

![Burning rate plot of Al-doped TiO₂ additives](image)

Figure 18. Burning rate plot of Aluminum-doped TiO₂ additives; D1 containing 3% and D2 containing 5% Al content within the TiO₂ nanoparticles which were added at 1.0%. For comparison, the 70% AP baseline, B1, and the curve fit for formulas C1:C2:C3 are also shown.

The doped study was conducted by using three separate elements to dope the TiO₂ additive; Al, Fe, and Gd (D1-D5, Table 1). All of the additives for the doped-TiO₂ study were synthesized using the modified sol-gel technique. The first plot, Fig. 18, shows two formulas that both have Al-doped TiO₂ but at different levels; D1 has 3% Al content within the TiO₂, and D2 has 5% Al content. In this plot, the two Al-doped formulas are seen displayed against their respective 70% AP binder, B1, and also against the burning rate curve fit from the other TiO₂ formulas that produced an anomalous
burning rate feature, formulas C1, C2, and C3. It can be seen that Formulas D1 and D2 both created a defined mesa burning rate between the other two curves shown and dropping below the baseline at high pressures. The increased Al doping level, D2, showed slightly lower burning rate magnitudes.

![Burning rate plot](image)

Figure 19. Burning rate plot of propellants containing 0.5% TiO$_2$ doped with 3% Al (D3), 3% Gd (D5), and 3% Gd (D5). Also plotted for comparison is the burning curve for the 80% AP baseline, B2.

The type of element used to dope the TiO$_2$ was varied in the last set of formulas shown in Fig 19, which all used 80% AP, 0.5% additive, and 3% doping; the respective 80% baseline, B2, was also plotted. Formula D3 contained Al-doped TiO$_2$ and was seen to follow very near to the curve of B2 which also was closely followed by formula C7 as shown previously, Fig. 19. Unlike formula C7, the burning rate of formula D3 suddenly jumps near 2000 psi (136.1 atm) up to the burning rate values similar to other doped
TiO₂ propellants at that pressure. The burning rate data from the other propellants, formula D4, which contained Fe-doped TiO₂, and from formula D5, which contained Gd-Doped TiO₂, can be seen in Fig. 19 to lie in the same area of scatter and so were represented by a single curve fit.
An explanation for the anomalous behavior of the baseline propellant B1 rests strongly on the low percentage of binder. Between the two 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. 13. This dependence on oxidizer loading corresponds well with Summerfield’s original observation wherein a decreased solid loading increases the chances of anomalous burning and the recurring proof in following studies.\textsuperscript{1,14,16} The burning rates shown here for 70% AP are in stark contrast to King’s burning rate\textsuperscript{18} 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 900 psi (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 since that pressure roughly aligns with and resembles regime II burning of AP as described by Boggs.\textsuperscript{20} However, since there was no major event at 2000 psi (136.1 atm) where regime III begins it is 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 and which indicates that the binder melt layer was more likely the responsible mechanism.\textsuperscript{27}

Other work by Price has focused on this same propellant formula, referred to as a coarse AP matrix in Price’s work. In one case, during testing to determine burnable limits, it was shown that this baseline formula successfully burned from atmospheric pressure up to 2000 psi (136.1 atm).\textsuperscript{28} In another study, 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.\textsuperscript{28} This result was most likely due to a slight difference in the exact AP particle size distribution, and none was supplied in Price’s publication.

By altering the crystal structure of the TiO\textsubscript{2} additive, no difference was observed in the overall burning rate curve, Fig 14. Using the premise that the change in the burning rate versus the baseline (B1) 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 C4, seen in Fig. 15, indicates that the additive has the ability to fully out-weigh the anomalous burning mechanism and return the propellant to normal burning behavior. The fact that C4 appears to be an extension of the initial burning curve of B2 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. This then indicates that formulas C1, C2, and C3 were acting as inert particles and simply affecting the viscosity which is in disagreement with Brill’s 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, C5 and C6, clearly showed drastically increased burning rates, thus indicating a catalytic enhancement of the burning rate (Fig. 16). Note that in Fig. 14 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 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 also sheds light on why there has 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 C7 to have very little effect on the burning rate at high solids loading (Fig. 17) and again points to a physical mechanism related to binder flow. This effect is in contrast to the anatase TiO$_2$ results in Fig. 16 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 (DSC) and TGA analysis of additives synthesized by the original sol-gel method
confirmed this conclusion.\textsuperscript{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, has proven that it is not always the case.

Preliminary DSC results (not shown herein) also indicated that doping TiO$_2$ would increase catalytic behavior. This result was rationalized by the change in surface properties and chemical composition of the additive particles as a result of the doping. Formulas D1 and D2 explored varying of the dopant levels of Al in the TiO$_2$; 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 suggests in his work that TiO$_2$ showed a reduction in the AP redox chemistry, and that this could lead to reduced burning rates.\textsuperscript{39} If the doping enhances this redox reduction, then it could explain the mesa burning. However, further testing would need to be conducted before a definitive solution can be stated. An extensive study relating DSC and TGA measurements to the burning rate results is currently underway in the authors’ laboratory and will be published in a future article.

Other doping elements were explored in formulas D4 (Fe) and D5 (Gd); when these are contrasted to Al doping in formula D3 at 80\% AP in Fig. 19, it is seen that they did not have the same effect as Al. Both D4 and D5 behaved similarly to C4, which was reasoned to indicate a higher emphasis on viscous effects than on a catalytic mechanism. D3, on the other hand, maintained burning rates similar to the baseline until higher pressures, where 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 definitively 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 above 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.
CHAPTER VI
CONCLUSIONS AND RECOMMENDATIONS

Presented within this work was a comprehensive review of past research 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 has inspired the current work which 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 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’s work,$^39$ although 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 discernable 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. Amongst the doping elements investigated, Al proved to be of most interest. To the author’s 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 next steps in experimentation can be considered. In regards to further propellant testing, 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. A need also arises to carry out further characterization of the additives to determine parameters that alter their reaction behavior and also to investigate this behavior itself with further DSC, TGA, and other instrument methods.
REFERENCES


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