

CATALYTIC NANOPARTICLE ADDITIVES IN THE COMBUSTION OF AP/HTPB
COMPOSITE SOLID PROPELLANT

A Thesis

by

KEVIN R. KREITZ

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2010

Major Subject: Mechanical Engineering

Catalytic Nanoparticle Additives in the Combustion of AP/HTPB Composite Solid

Propellant

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Approved by:

Chair of Committee,	Eric Petersen
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ABSTRACT

Catalytic Nanoparticles in the Combustion of AP/HTPB Composite Solid Propellant.

(December 2010)

Kevin R. Kreitz, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Eric Petersen

Presented in this thesis is a study of the effects of nano-sized particles used as a catalytic additive in composite solid propellant. This study was done with titanium oxide (titania)-based particles, but much of the findings and theory are applicable to any metal oxide produced by a similar method. The process required for efficiently producing larger batches of nanoparticle additives was seen to have a significant impact on the effectiveness of the additive to modify the burning rate of composite propellant consisting of ammonium perchlorate (AP) and hydroxyl terminated polybutadiene (HTPB). Specifically, titania was seen to be both an effective and ineffective burning rate modifier depending on how the nanoparticle additive was dried and subsequently heat treated. Nanoadditives were produced by various synthesis methods and tested in composite propellant consisting of 80% AP. Processability and scale-up effects are examined in selecting ideal synthesis methods of nanoscale titanium oxide for use as a burning rate modifier in composite propellant. Sintering of spray-dried additive agglomerates during the heat-treating process was shown to make the agglomerates difficult to break up during mixing and hinder the dispersion of the additive in the

propellant. A link between additive processing, agglomerate dispersion mechanics and ultimately catalytic effect on the burning rate of AP/HTPB propellants has been developed by the theories presented in this thesis. This thesis studies the interaction between additive dispersion and the dispersion of reactions created by using fine AP in multimodal propellants. A limit in dispersion with powder additives was seen to cause the titania catalyst to be less effective in propellants containing fine AP. A new method for incorporating metal oxide nanoadditives into composite propellant with very high dispersion by suspending the additive material in the propellant binder is introduced. This new method has produced increases in burning rate of 50 to 60% over baseline propellants. This thesis reviews these studies with a particular focus on the application and scale-up of these nanoparticle additives to implement these additives in actual motor propellants and assesses many of the current problems and difficulties that hinder the nanoadditives' true potential in composite propellant.

ACKNOWLEDGMENTS

I would like to first thank my academic/research advisor and committee chair, Dr. Eric Petersen, for his guidance and dedication that goes well beyond what is required of him. I would also like to thank Dr. Tahir Cagin and Dr. Devesh Ranjan for serving on my thesis committee.

I would like to thank my many friends and colleagues at the Turbo-Machinery Lab, especially those who have worked with me on this project: Mathew Stephens, Corey Frazier, Jeffery Johnson, Tyler Allen, Tom Sammet, and Mitch Johnson. Much of this work would not be possible without the material science expertise of David Reid and Dr. Seal from the University of Central Florida. Discussions with U.S. Army AMRDEC personnel at Redstone Arsenal (Christi Dolbeer, Amy Gerards, and Larry Pledger) and AFRL (Dr. George Harting, Edwards AFB) with regard to the use of the scaled-up additives in large propellant batches are much appreciated. I would like to thank the Missile Defense Agency for funding under MSTAR contract number HQ0006-05-C-0023, with Dr. Pashang Esfandiari as the technical monitor. I would also like to thank the Texas Engineering Experiment Station for additional funding.

Finally, I would like to thank my family for their continued support. Without the aid of my loving parents, Glen and Denise Kreitz, I would not be where I am today, so to them I give many thanks.

NOMENCLATURE

AP	Ammonium Perchlorate
HTPB	Hydroxyl Terminated Polybutadiene
r	Burning Rate
P	Pressure
a	Temperature Coefficient
n	Combustion Index
σ_P	Temperature Sensitivity of Burning Rate
π_K	Temperature Sensitivity of Pressure
K	Ratio of Burning Surface to Nozzle Throat Area
DSC	Differential-scanning Calorimetry
TGA	Thermogravimetric Analysis
LTD	Low-temperature Decomposition
HTD	High-temperature Decomposition
AMPAC	Advanced Materials Processing and Analysis Center
UCF	University of Central Florida
TAMU	Texas A&M University
SEM	Scanning Electron Microscope
TEM	Transmission Electron Microscopy
IPDI	Isophorone Diisocyanate
ESD	Electro Static Dissipating
XRD	X-Ray Diffraction

f_c	Catalyzed Reaction Fraction
DOA	Dioctyl Adipate
D_{Agg}	Agglomerate Dispersion Size
D_{AP}	AP Dispersion Size

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1. INTRODUCTION

Solid propellant is a self-sustaining combustible material containing both fuel and oxidizer in a solid state. In composite solid propellant, the oxidizer is a solid crystal particle of various sizes that is mixed into long hydrocarbon chains that are polymerized into rubber providing the fuel. The most common oxidizer crystal used in composite propellant is ammonium perchlorate (AP). Composite solid propellant is widely used in several applications such as gas generators for airbags, propulsion for large space vehicles and tactical missiles, attitude control systems, and as pressure generators in deep sea oil operations. Most applications of solid propellant only require a simple mechanical design. For example, when used in rocket motors, solid propellant is stored in the combustion chamber, and the burned gaseous products are exhausted through a nozzle creating thrust from a relatively simple design that requires no moving parts like those required by liquid propellant systems. However, the drawback to this simple system is the lack of in-flight throttling that is seen in liquid propellant systems, and it is for this reason it is important to understand the exact combustion characteristics of solid propellants to create safe and efficient applications of solid propellant.

Tailoring propellants is a common goal in the propellant community that involves adjusting the propellant formulation or the addition of additives (NASA, 1967). The ability to take existing formulations and disperse small amounts of additives, 1% by weight, throughout the propellant grain and modify the combustion characteristics of the

This thesis follows the style of *Combustion, Science, and Technology*.

propellant while keeping similar physical properties can be very useful. Tailoring allows a wide array of propellants to be developed quickly and efficiently.

Advances in materials science and engineering have made the use of nanoparticles feasible in several applications. The increase of surface-area-to-mass ratio, produced by the reduction in diameter, in conjunction with the ability to engineer particles with different surface chemistry present many favorable characteristics for combustion. These advances have led to much research to investigate the use of nanoparticles in composite propellant for various purposes. Through the addition of nano-scale metal oxide additives to composite solid propellant, it is possible to modify burning rate and achieve propellant tailoring (Stephens et al., 2010). Controlling the composition, morphology, and amount of these additives in the formulation of solid propellant allows the propulsion community to develop propellants with specific combustion characteristics. Such additives at mass loadings of 1% or even less can modify propellant in several ways including affecting material properties, partaking in the combustion process, or acting as catalysts. Characterization of how these additives affect propellant combustion can provide important information needed to tailor the burning rate of solid propellant to that desired by specific applications.

The use of nanoparticles as additives in solid propellant has many inherent benefits. First, the increase of surface area-to-mass ratio produced by the reduction in diameter has been shown to be favorable for affecting the combustion process through catalytic activity (Fujimura and Miyake, 2009). Second, nanoparticles can be synthesized from the ground up to have specific surface chemistry and crystal structure.

This ability to engineer particles allows for more customization and tailoring of propellant formulations when compared to conventional, micron-scale additives. With the increasing technologies associated with nanoparticles, they have become much more practical for use in the propellant and combustion fields. Laboratory-scale demonstrations using small samples of propellant are useful for diagnosing the effectiveness of nano-scale additives. However, when scaling up the propellant to larger, more realistic batches, the larger amount of additives required to realize a comparable mixture to those tested in the laboratory will most likely require the nanoparticles to be processed in a manner that is not exactly the same as utilized in the lab-scale experiments.

These types of scale-up studies are not only necessary from a material synthesis point of view but also from the solid propellant aspect. The burning rate of propellants has been known to vary when used in larger rocket motors (Fry, 2001). In actual motors, small changes in burning rate can translate into a large difference in specific impulse (Miller, 1971). Large-scale-batch burning rate validation tests and scaled motor tests have been conducted on the additives and formulas presented in this thesis. The investigations presented in this thesis were a necessary, preliminary step to make the motor-scale tests possible. However, the results of the larger-batch tests are not presented in this thesis.

This thesis presents recent work with nano-scale titanium oxide (titania) as a burning rate modifier in composite propellant consisting of ammonium perchlorate (AP) and hydroxyl terminated polybutadiene (HTPB). The work investigates particle

processing, agglomeration, dispersion, and scale-up that will be important for practical application of these additives. Additionally the effects of changes in propellant formulation for scale-up are investigated. New alternative methods of additive dispersion are investigated. Provided first is a background on the use of additives and catalysts in composite propellant, followed by details on the additives, propellants formulations, constituents, and testing procedure. Following a summary of each experiment is a discussion on the possible mechanisms for the observed behaviors.

2. BACKGROUND

2.1 Burning Rate of Solid Propellant

The combustion of solid propellant is typically evaluated by how its burning rate changes as a function of pressure, which is an important parameter in propellant motor design. This relationship between burning rate and pressure is traditionally expressed by the power function in Equation 1, where r is the burning rate, P is the chamber pressure, a is an empirical constant influenced by ambient grain temperature that is sometimes called the temperature coefficient, and the burning rate exponent n , which is sometimes called the combustion index (Sutton and Biblarz, 2001). This power law is also known as the St. Roberts' or Vieille's law. When plotted on a log-log plot, propellants that follow this law will exhibit a linear relationship between burning rate and pressure.

$$r = aP^n \quad (1)$$

The burning rate exponent, n , determines how sensitive the burning rate of a propellant is to pressure change. In addition to pressure, temperature can affect the burning rate of a propellant and this would be reflected in changes in the constant a . The sensitivity of burning rate to temperature can be expressed by temperature coefficients. Equations 2 and 3 show two of the most common temperature coefficients, temperature sensitivity of burning rate (σ_p) and temperature sensitivity of pressure (π_k) (Sutton and Biblarz, 2001).

$$\sigma_p = \left(\frac{\delta \ln r}{\delta T} \right)_p = \frac{1}{r} \left(\frac{\delta r}{\delta T} \right)_p \quad (2)$$

$$\pi_K = \left(\frac{\delta \ln P}{\delta T} \right)_K = \frac{1}{P} \left(\frac{\delta P}{\delta T} \right)_K \quad (3)$$

Where T is temperature, P is pressure and K is a geometric function, namely the ratio of burning surface to nozzle throat area. These temperature coefficients express how much a differential change in initial temperature affects the burning rate at a constant pressure or the pressure increase at a constant K . The two temperature coefficients can be related by the Equations 4 (Sutton and Biblarz, 2001). More details on effects of temperature on the burning rate of solid propellant can be found in a report by Kishore and Sridhara (1986).

$$\pi_K = \frac{1}{1-n} \sigma_P \quad (4)$$

The burning rate of a specific propellant can be determined from a variety of experimental tests. Currently, there have been many breakthroughs in modeling the burning of solid propellant, but it is not yet possible to accurately predict the burning rate of new propellant formulations from a purely theoretical origin. Therefore motor designs rely heavily on empirical data collected from experimental setups such as the strand bomb, which is discussed later in this thesis.

The burning of solid propellant is also heavily dependent on several parameters related to the oxidizer particle, AP, used in the formulation, such as particle size, distribution, loading. The mass loading of AP in a solid propellant formulation affects the fuel-to-oxidizer ratio, which changes the adiabatic flame temperature and ultimately the burning rate. Figure 1 shows how variations of AP mass loading in an AP/HTPB

propellant change the flame temperature, which is calculated using the ProPep software (Cruise, 1979).

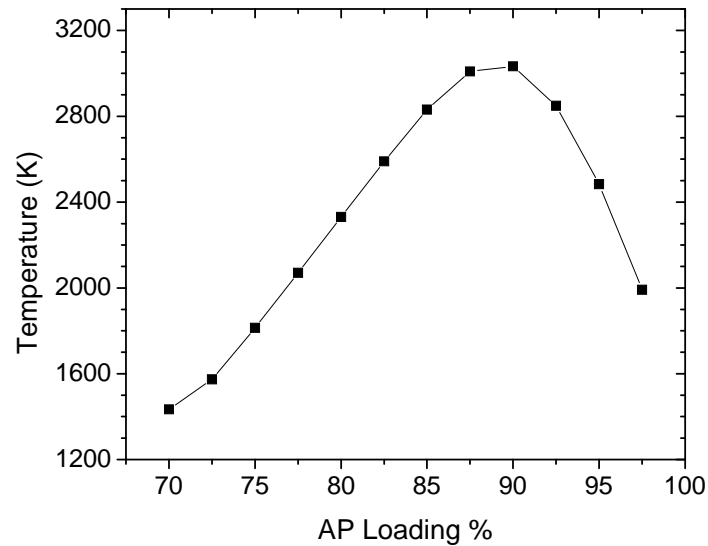


Figure 1. Flame temperature of AP/HTPB propellant for different AP percentages.

The burning rate of composite solid propellant is dependent on the particle size of the AP crystals. Propellants with smaller AP particle size will have a higher burning rate, where larger AP will result in a slower burning rate. This behavior is due to the smaller AP or fine AP being better mixed within the binder creating a more premixed flame, and the propellant with the large AP particles burns more like a diffusion flame. Figure 2 shows how changing particle size will vary burning rate (Jeppson et al., 1998). A major breakthrough in propellant modeling came from a paper by Beckstead et al. (1970) that modeled the burning AP propellants as three flames and was able to capture

this relationship between particle size and burning rate. This model became known as the BDP model and has since become the basis for many current propellant models.

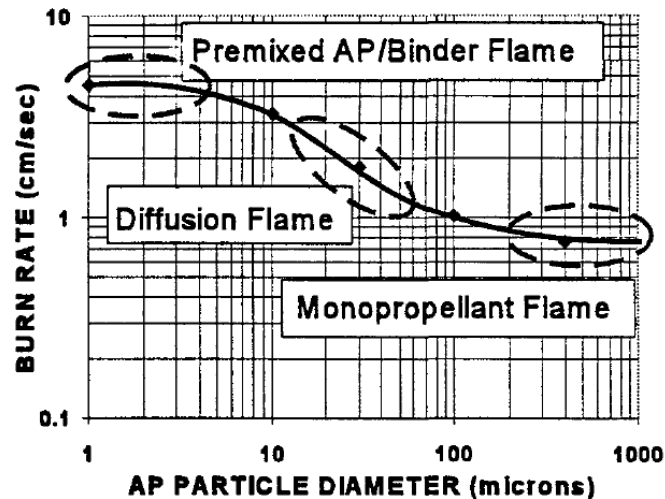


Figure 2. Combustion regimes and effect of particle size on the burning rate of monopropellant AP (Jeppson et al., 1998)

Solid propellant can contain one size of oxidizer particles, a monomodal propellant, a blend of two sizes, bimodal, or several sizes of particles, multimodal (Renie et al. 1978). When multiple sizes of oxidizer particles are used in a propellant, smaller oxidizer crystals are used to fill the space between larger crystals and hence increase the total amount of oxidizer while maintaining a viable physical propellant. Increasing the portion of small or fine particles in comparison to the portion of large or coarse particles will increase the burning rate (NASA, 1967).

Small changes in the parameters of the AP can change the way a propellant reacts. More details on the dependence of AP are reported by Price (1998). All of these

sensitivity parameters not only affect the burning rate but also how effective the additive is. Care must be taken to modify propellant formulations in a controlled way such that changes in burning rate are understood, due to the numerous parameters that can affect burning rate.

2.2 Additives for Solid Propellant

Additives for composite solid propellant add additional complexity to an already complicated system and have been the focus of many research studies for numerous years. Early work with additives for solid propellant involved micron-sized additives, but with the increase in technologies it is now practical to use nano-sized additives. There are several reviews on additives for AP/HTPB propellants which are referenced in this thesis. The most common types of additives used in solid propellant are inorganic oxides such as the additive used in this study, titania, which is considered to be a catalyst. However, there has been some interesting work with organic additives such as melamine (Stoner and Brill, 1991). A common method for studying a catalytic additive for composite propellant is to measure the decomposition of AP-catalyst pellets, but as questioned by Boggs et al. (1988) this approach may not directly relate to the performance of an additive in the actual combustion of propellants. This method for studying how catalysts affect the combustion of solid propellant only accounts for the solid decomposition and does not account for the gas phase reactions where much of the catalytic activity may take place.

Ammonium perchlorate has been shown to have two steps in thermal decomposition, which can be seen in differential-scanning calorimetry and thermogravimetric analysis (TGA). The two steps are known as the low-temperature decomposition (LTD), which is an exothermic reaction, and the high-temperature decomposition (HTD), which is an endothermic reaction involving the simultaneous dissociation and sublimation of AP to HClO_4 and NH_3 (Jacobs and Whitehead, 1969). It has been shown by Lang and Vyazovkin (2006) that the HTD can become exothermic if there is a catalytic surface for the produced gasses to undergo an oxidation reduction.

In addition to studies that investigate the effects of catalysts on the thermal decomposition of AP, there have been studies that investigate the effects of additives on actual propellant formulations. Knowing that metal oxides are good catalysts in the oxidation of high polymers, Rastogi et al. (1977) studied the effect of additives on the burning rate of composite solid propellant and suggest that enhanced flame temperature is due to accelerated reactions in the gas phase, which results in an increase in burning rate. However it is unlikely the actual flame temperature is increased since the additives do not partake in the reactions and heat is taken away from the reaction to heat the additives, which are essentially inert. It is however possible that the accelerated reactions create an increased surface temperature (rather than flame temperature), which increases burning rate.

A common approach to modeling or visualizing the combustion of solid propellant is to divide the system into three regions: the solid phase, the condensed-mixed phase, and the gas phase (Beckstead et al., 2004). Each phase interacts with

another through mass flow and heat transfer. The combustion that takes place in the gas phase provides the system with a heat source. This heat combined with the pressure of the system cause decomposition and melting of the solid phase into the condensed-mixed phase and eventually producing the gas phase. These gas products in turn feed the combustion taking place in the gas phase. Figure 3 shows a schematic of these regions in a propellant. When a catalyst is added to the propellant, accelerating the reactions in the gas phase, it is possible for the reacting gas phase to be smaller and get hot faster, which produces more heat that is transferred into the condensed phase, increasing burning rate.

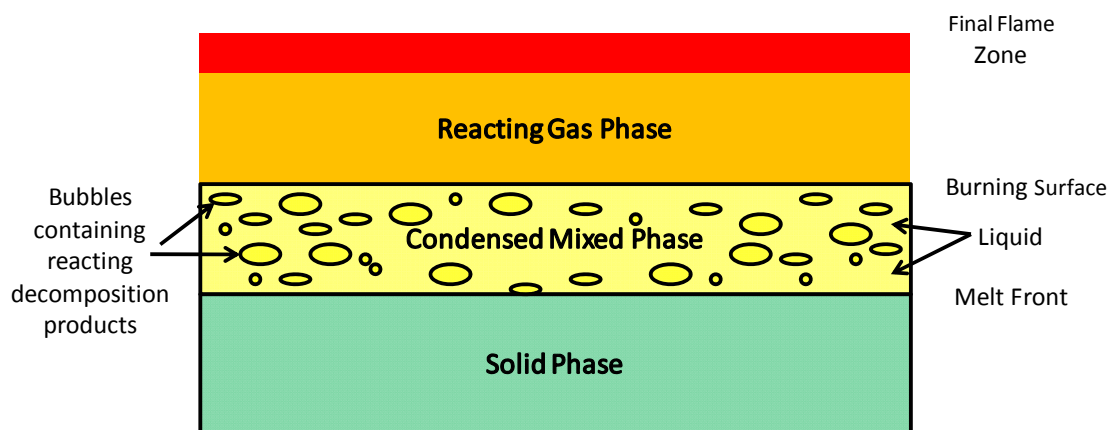


Figure 3. Three-phase model of propellant combustion.

Two common metal oxides studied as catalysts for AP-HTPB propellants are titanium oxide and ferric oxide. Extensive work on ferric oxide (iron oxide) has been done by Strahle et al. (1972), Handley and Strahle (1975), and Chakravarthy et al. (1997). In these studies, the combustion of composite propellant is tested by a sandwich method, where additives are placed in a thin strip between pressed AP and binder. This

setup is used to evaluate both chemical and physical phenomena in the combustion of composite propellant.

Titanium oxide (titania) has been investigated in several studies as an additive for composite propellant. These studies have investigated titania as a catalyst to the thermal decomposition of ammonium perchlorate as well as to the reactions between binder and oxidizer. Titania's effect on propellant burning rate has also been studied, and the results have led to a variety of different conclusions. Some studies have even described titania as inactive or less active: e.g., Ramamurthy and Shrotri (1996), and Pearson (1971). In recent work by Stephens et al. (2010) and Reid et al. (2007), TiO_2 has been shown by a parametric study to increase the burning rate of composite propellant with particle sizes at both the nano- and micro-scale. Titania has also been implemented to promote plateau burning by Stephens et al. (2009). Plateau-burning propellants are defined as propellants that have a pressure range where burning rate is constant, where normal propellants would otherwise show an increase in burning rate as pressure increases. Although the present paper focuses on non-plateau-burning propellants, in both published and unpublished studies the author has not seen the addition of titania change a non-plateau-burning propellant into a propellant with a plateau.

Work by Solymoi and Fonagy (1967) as well as Boggs et al. (1988) found titania to have little to no increase in burning rate of composite propellant. Boggs et al. reported a decrease in deflagration rate of AP with the presence of titania additives. However, these experiments were conducted with micron-sized particles at loadings of 2 and 8 %. The results presented later in this report are for titania additives synthesized at the nano-

scale and used at loadings of 1% or less. The additives Boggs et al. (1988) reported to be good burning rate modifiers produced a burning rate increase of 20-30%.

There have been several studies that have investigated how titania could affect the combustion of solid propellant. In an investigation of plateau-burning propellants, TGA showed that the weight loss of AP was faster in the presence of titania (Freeman et al., 1998). In a characterization of the thermal decomposition of AP with and without titania catalysts, titania was shown to affect the high-temperature decomposition of AP (Fujimura and Miyake, 2009) similar to most catalysts previously used in solid propellants. These studies show empirical evidence, both from burning rate studies as well as AP thermal decomposition studies, that titania can have catalytic effects on the combustion of composite propellant.

When reviewing the literature, one can conclude there are inconsistencies with regards to titania as an effective additive. Some research has shown it to be effective, while others show evidence that it is not effective. The present study uncovers why different results might be seen with seemingly the same titania additive when synthesized on a nano-sized scale. Additionally, the work previously reported in literature is for small-scale laboratory results, both burning rates and thermal decomposition studies that may not translate directly to a scaled-up environment. There is a need for research into the details needed to fully utilize any metal oxide nanoparticle additives, not just titania, in solid propellant. The implementation of these nano-additives is not as simple of a process as it may seem and often is problematic in application and large quantities. Often the formulations used for laboratory-scale tests of

burning rate are simplified versions of AP/HTPB formulations, such as modifications to physical properties, and this simplification may create unknown effects of the additives' ability to tailor combustion. More importantly, modifications to the production of additives that may not seem to cause any change in the final additive but ultimately do change how the additive performs in a propellant. For example, in an initial attempt to produce scale-up additives for a large motor firing of nano-titania catalyzed solid propellant, additives that were expected to perform well ultimately showed no effect. Figure 4 shows a plot of strand bomb burning rates of what was expected from the addition of titania and how well the additive produced for scale-up performed compared to a baseline propellant. More information about these kinds of tests and results thereof are presented later in this thesis, but this result is an example of how the scale-up of propellant additive is not a trivial process.

In addition to producing important scale-up information, these scale-up investigations add valuable knowledge to the underlying physical and chemical understanding of additive behavior in actual solid propellant grains and in motor configurations.

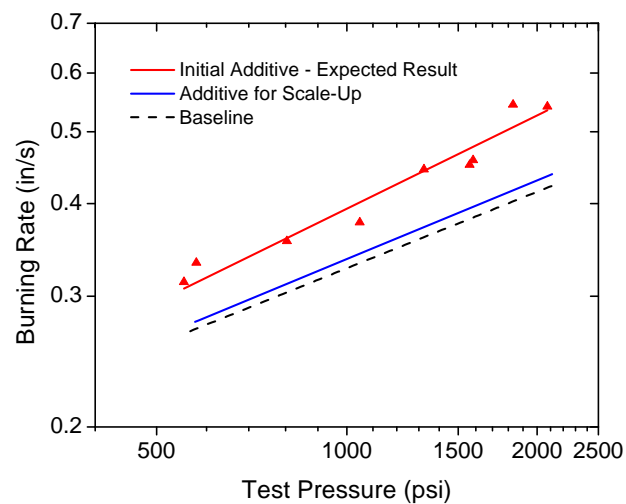


Figure 4. Pressure dependence of the burning rate for an initial scale-up of Al-doped titania additive at 1% in a 80% monomodal propellant, an example of problems that can occur from the scale-up of nanoadditives in composite propellant.

3. ADDITIVES AND PROPELLANT

One benefit of the present study is the ability to examine the full process of testing additives' effects on solid propellant burning rate from start to finish. The additives are synthesized in a controlled way by the Advanced Materials Processing and Analysis Center (AMPAC) at the University of Central Florida (UCF) and sent to the solid propellant research facility at Texas A&M University (TAMU). The additives are then formulated into composite solid propellant samples and tested. This procedure allows the research team to examine additive production, propellant mixing, sample production, burning and testing for effects on combustion outside the range of other research. For example, this collaboration minimizes uncertainty and unknown variables that can occur with purchased additives while still being able to fully analyze the effects on burning rate. The propellant processing and burning rate results can then directly impact the details of future additive synthesis in a timely manner.

3.1 Additives

Based on previous work that showed nano titania produced in the authors' laboratory to be an effective additive for composite propellant (Stephens et al. 2010) (Reid et al., 2007), nano titania was selected for a scale-up study. In addition to pure titania, various doping of titania was used including Fe and Al. These additives were studied in non-metalized propellant formulations first at the laboratory scale and then in a scaled-up rocket motor environment. For such a test, the additives must be produced in

quantities several times larger than the amount needed for laboratory-scale testing. Testing the particles made for the larger batch first in a lab-scale setting gave the opportunity to quickly examine the effects such a scale-up process would have on the titania additives' performance.

Additives used in this study were synthesized by the sol-gel method, which allows for detail control of several properties of the particles. Titanium isopropoxide was hydrolyzed in an ethanol/water mixture, and the suspension was held at elevated temperature (84 °C) to promote crystallization. TiO₂ powders were obtained by centrifugation followed by drying with a rotary evaporator and grinding by hand with a mortar and pestle. The powders consisted of agglomerates of anatase nanoparticles with a 5-nm average crystallite size and a small amount of amorphous content. The powders were then heat-treated at 400 °C for 3 hours to ensure full crystallization to anatase was achieved, and during this process the nanocrystallite size grew to 7 nm.

The method for synthesizing the scaled-up titania additives was modified to accommodate for the larger quantity of additives. The scaled-up synthesis method stayed essentially the same except the particles were spray dried instead of being dried with a rotary evaporator (rotovapped). After the drying process, the additives were heat-treated just as they were for previous experiments at 400°C for 3 hours. The spray drying process allows for faster and more uniform additive production because the particles do not need to be ground with a mortar and pestle like the additives that are dried in the rotary evaporator. Additionally, the spray drying process produces spherical agglomerates with a narrow size distribution as shown by the scanning electron

microscope (SEM) images in Figure 5. The process using the rotary evaporator followed by grinding generates random-shaped agglomerates with a very wide size distribution. SEM images of the rotovapped titania additives are shown in Figure 6. In addition to being more-homogeneous agglomerates, the spray-dried particles have excellent flow properties and create minimal dust. These attributes are considered to be a product of the agglomerates' smooth spherical shape, and make the additives easier and safer to work with than other types of nanoparticle materials, such as conventional nano-aluminum, especially in large-scale processing.

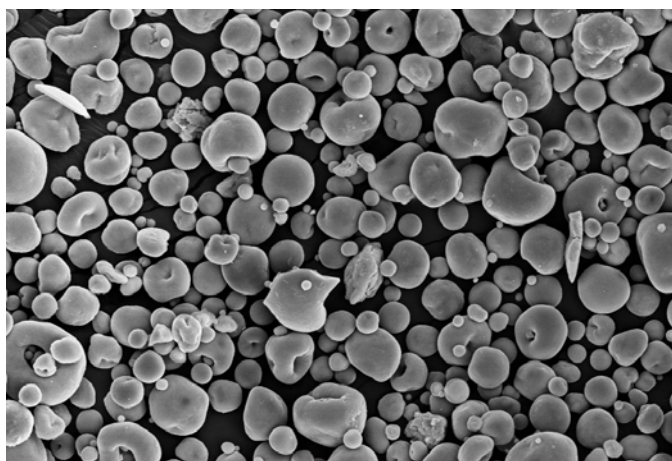


Figure 5. SEM image of heat-treated additives produced with the spray-drying method.

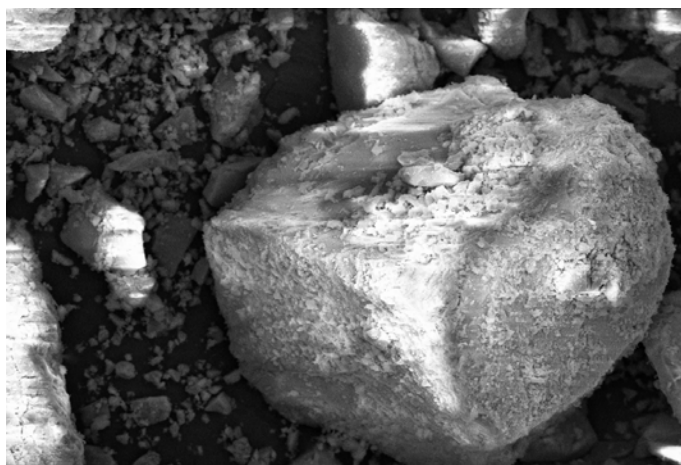


Figure 6. SEM image of heat-treated titania additive dried with a rotary evaporator then ground.

It is important to note, the images in Figure 5 and Figure 6 show agglomerates of several particles of the titania additive. The agglomerates are made up of several nano-sized particles that have clumped together. In an actual application of nanoparticles in a propellant, some agglomeration would be unavoidable, so it is important to understand how different agglomerations could be more beneficial for actual use in a propellant. The TEM (Transmission Electron Microscopy) image in Figure 7 shows the individual particles that make up the agglomerates.

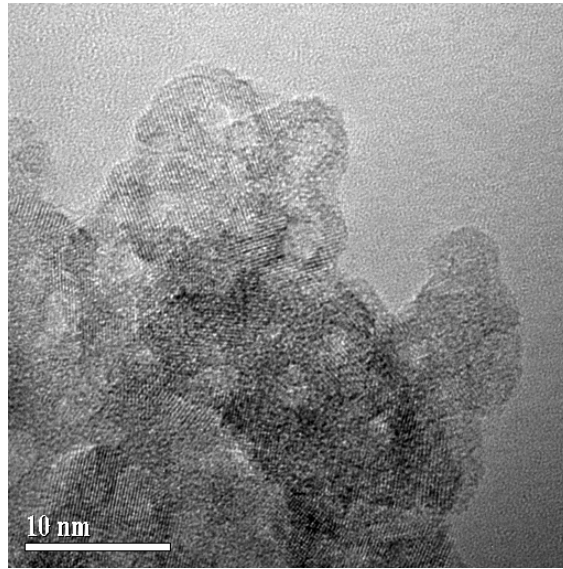


Figure 7. TEM image of a titania agglomerate showing the individual particles that combine to make the agglomerate.

3.2 Propellant Mixing

All of the propellant samples prepared for the studies presented in this thesis were produced by a hand mixing method that has been compared with good agreement to a mechanical mixing method, which simulates large-scale industrial mixers (Stephens et al., 2007). The general procedure is described as follows. Twenty grams of propellant are produced in a beaker for each propellant batch. First, the binder is developed by mixing the proper masses of all binder ingredients except the curing agent for several minutes in a beaker. Then the binder is placed in a desiccator and vacuumed to remove air voids that have developed while mixing. The binder is held under vacuum for at least 45 minutes until all voids have been removed and one transparent, homogeneous mixture remains. One must be careful when vacuuming the binder not to decrease pressure too

quickly or the binder will violently flow out of the beaker and the measured masses will become incorrect. In the case of simple AP/HTPB propellants, this binder would only consist of HTPB and therefore does not require mixing and vacuuming. To the binder, solid particles are added in order of size from largest to smallest, starting with coarse AP. This order has been found to produce an even distribution of ingredients without drying out the propellant. After massing the correct amount of a solid constitute and adding it to the propellant, the mixture is mixed with a glass stirring rod for a minimum of ten minutes until a uniform propellant is formed. One must be careful to thoroughly mix any propellant that may stick to the side of the beaker or glass stirring rod. Between the additions of each solid constitute, the propellant is placed in a desiccator and vacuumed for two hours to once again remove any voids that have developed while mixing and bring the binder and particles into intimate contact. When powder additives are added to the propellant, they are mixed in the same manner as other powder ingredients, and since they will have a smaller size than any of the AP particles they would be added last followed by proper mixing and vacuuming. Using a pipette, the curing agent isophorone diisocyanate (IPDI) is added to the propellant and mixed as before for ten minutes then placed in the desiccator and vacuumed for 20 minutes. During this time the HTPB chains are beginning to be linked together by the IPDI forming a stiff rubber matrix and if allowed to sit in the desiccator for too long, the propellant will cure and be unable to be extruded to complete the propellant sample. The maximum time a propellant can sit after mixing the IPDI and still be able to extrude the propellant is about 40 minutes.

The propellant test samples are prepared by allowing the propellant to cure in a 6.35-mm (0.25 in) Teflon tube which has an internal diameter of 4.76-mm (0.1875 in). To get the propellant into the tubing, the propellant is first placed into a syringe where it is once again placed under a vacuum. The plunger to the syringe is not allowed to compress, until 3 minutes of vacuuming. Then, the plunger is allowed to compress, slowly compacting the propellant free of air voids. Depending on the viscosity of the propellant, it is then either injected into the Teflon tubing, or if the viscosity is too high the plunger is removed and the propellant is pressed into the tubing. The propellant samples are then placed into an oven to finish curing at 63°C for one week. Once cured, the propellant samples are removed and stored in a licensed propellant magazine until needed for testing.

The hardness of the propellant may be adjusted in the propellant formulation by adjusting the cure ratio, which determines the ratio of HTPB to IPDI. For HTPB-based binders, the cure ratio is defined as the ratio of –NCO groups in the IPDI to the –OH groups in the HTPB as shown in Equation 5. In practice, it more useful to have the ratio in terms of the mass ratio, which can be expressed by the mass fraction of IPDI divided by IPDI's equivalent weight all over the mass fraction of HTPB divided by HTPB's equivalent weight as shown in Equation 6.

$$\text{Cure Ratio} = \frac{-NCO}{-OH} \quad (5)$$

$$\text{Cure Ratio} = \frac{m_{IPDI} / Eq.Wt_{IPDI}}{m_{HTPB} / Eq.Wt_{HTPB}} \quad (6)$$

As stated previously, the particle size and distribution of AP used in the formulation of solid propellant is very important. The AP used for the propellants in these studies was purchased from FireFox inc. at 200 microns. The AP was sized using imaging software on digital photographs of individual particles taken on an optical light microscope and stage micrometer. The AP particles were determined to have an average size of 193 μm with a standard deviation of 77 μm . A histogram of the AP particle size distribution is shown in Figure 8.

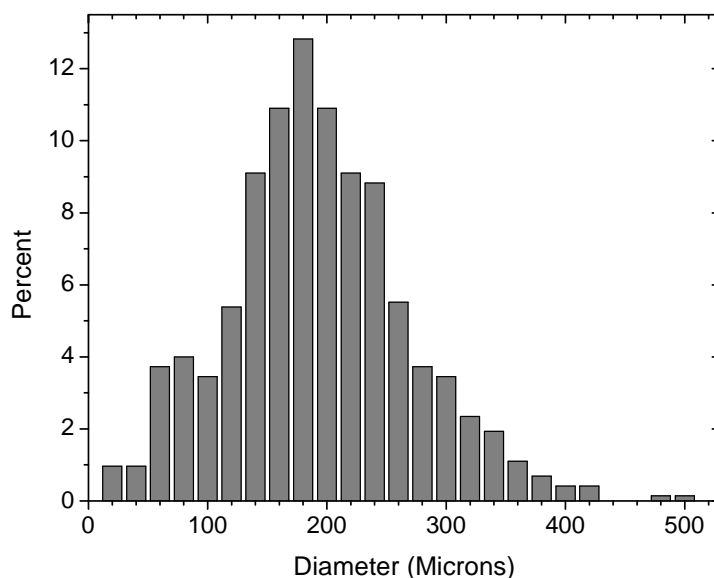


Figure 8. Ammonium perchlorate particle size distribution.

Due to the complex nature of the combustion of propellant, when evaluating the effectiveness of an additive the propellant is compared to a baseline formulation. The baseline is a propellant formulation with the same oxidizer-to-fuel ratio as the propellant with the additives, but without the presence of the additive. For example, a propellant

with 80% AP and 20% IPDI-cured HTPB binder would be used as a baseline to compare a propellant with 1% additive, 79.2% AP and 19.8% IPDI-cured HTPB binder.

4. EXPERIMENTAL TESTING

4.1 Strand Bomb Testing

The propellant samples presented in this thesis were tested at the solid propellant testing facilities at Texas A&M University, located at the Turbomachinery Laboratory. This facility is able to burn samples of propellant in a controlled environment at elevated pressures. The burning facility is designed to determine how the combustion properties, namely the burning rate, of solid propellant vary for different formulations. Over the past few decades, there have been many breakthroughs in modeling the combustion of solid propellant, but the primary method for designing new propellants remains empirical testing. The high-pressure burning facilities implemented at Texas A&M University are capable of conducting this type of empirical testing on solid propellant.

Once a new formulation is created, extruded into samples, and cured the propellant is ready to be burned. For each formulation, several samples of approximately one gram are burned inside a pressure vessel known as a strand bomb. The strand bomb is a cylindrical vessel, 12 inches long and 6 inches in diameter, made of a low-carbon steel alloy. Propellant samples can be burned in the strand bomb up to pressures of 5,000 psi (340 bar). This pressure range allows the characterization of the combustion of solid propellant as a function of pressure at high pressures. The strand bomb is capable of being oriented in a horizontal or vertical position and contains four optical ports. Three of the optical ports are located on the side of the strand bomb to give a view of the propellant regressing as it burns. The fourth optical port is located at the top of the strand

bomb and aligned concentric to the burning surface of the propellant sample. These optical ports allow the use of several optical diagnostic tools including: a broadband photoreceiver, spectrometer, and high-speed camera. Figure 9 and Figure 10 show the setup of the strand bomb in the more common vertical position. In addition to optical diagnostics, the strand bomb is equipped with three pressure transducers.



Figure 9. High-pressure strand burner at Texas A&M University.

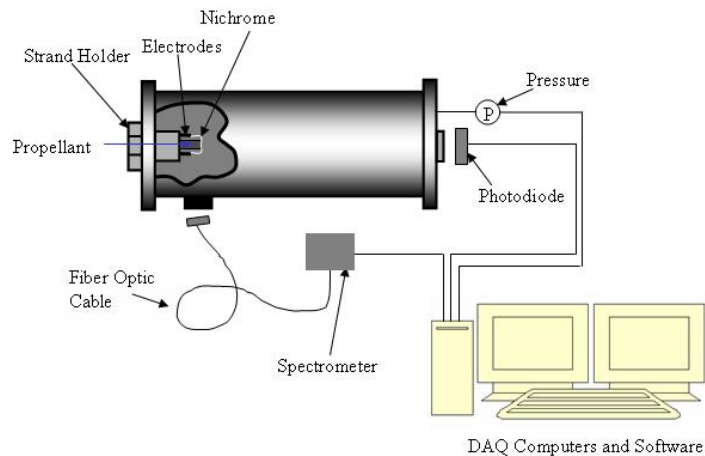


Figure 10. Schematic of strand bomb and data acquisition equipment.

The facility is designed to maximize the safety of those conducting the experiment. The high-pressure strand bomb is located inside a test cell constructed of reinforced concrete with a reinforced steel door. For safety, the circuit to ignite the propellant is connected to a relay that is triggered from the control room once the test cell has been evacuated. In addition to controlling ignition, the control room is able to remotely control the pressure in the strand bomb. This protocol ensures no technician is present in the test cell while the strand bomb is pressurized. The test cell containing the strand bomb is shown in Figure 11. Several aspects of the facility are designed to prevent any electro-static discharges from causing an unexpected ignition of propellant or any of its constituents. The use of conductive-soled shoes and a special electro static dissipating (ESD) coating on the floor keep the researchers grounded and prevent the build of any static charge.



Figure 11. Strand bomb test cell.

Propellant samples are cut into 1-in (25.4-mm) long samples. Approximately 10 samples are tested per batch. The tangential sides of the cylindrical samples were coated in a thin layer of inhibitor (liquid HTPB) to ensure proper end burning. Once a propellant sample is in place, the vessel is purged and filled with Argon to the test pressure, the sample is ignited. Ignition is achieved by passing high current through nichrome wire that is placed across one end of the sample.

During the burn of a sample of propellant, two data acquisition computers, located in the control room, are used to record the stand bomb pressure, the signal from the broadband photoreceiver, and spectrometer data, all as a functions of time. The burning time was determined by the inflection points in the pressure signal and validated by the photodiode's time history of the flame's visible emission. Typically the pressure rise within the chamber is observed to not exceed 10% of the initial pressure. The

recorded burning rate measurement for each test corresponds to the average pressure seen during the burn. Figure 12 shows sample pressure trace and photoreceiver signal.

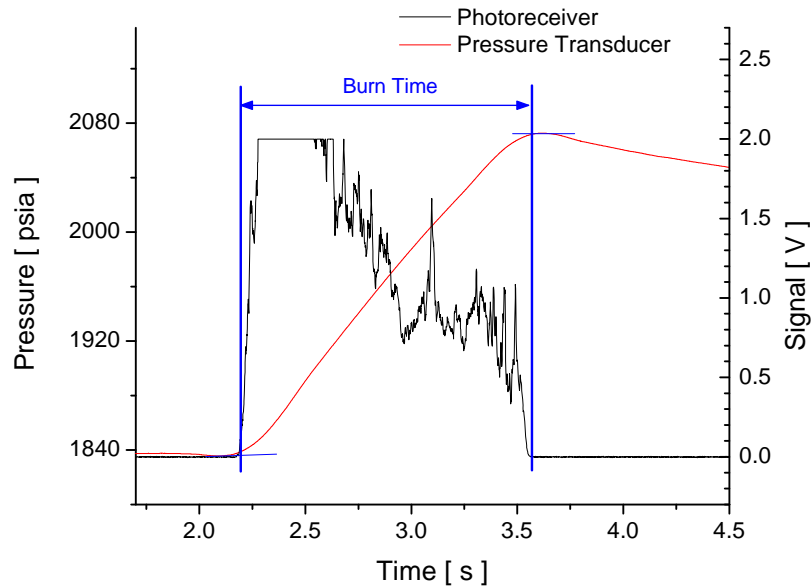


Figure 12. Example of how the pressure trace and photoreceiver signal are used to determine the burn time of a propellant strand.

Knowing the length of the sample, which is measured with a digital caliper before testing, and its burn time, the burning rate of the propellant can be calculated. As shown in Equation 7, the burning rate is the sample length divided by the burn time. Several samples are tested at varying initial pressures, and the burning rates are plotted as a function of pressure on a logarithmic plot. For the tests presented in this thesis, pressure was varied from 500 psi to 2000 psi. Typical propellant formulations will

exhibit a linear relationship on the logarithmic plot. An example logarithmic plot of burning rate as a function of pressure is shown in Figure 13.

$$r = \frac{\Delta X}{\Delta t} \quad (7)$$

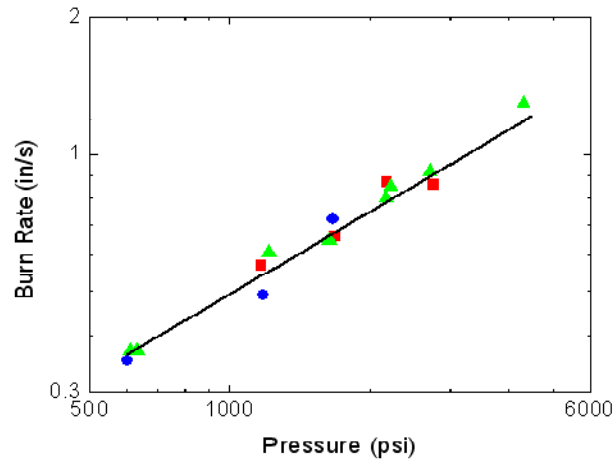


Figure 13. Example of a logarithmic plot of burning rate as a function of pressure for an AP-HTPB composite propellant. The different colors represent different batches of the same propellant, showing repeatability.

The logarithmic linear relationship between pressure and burning rate can be expressed by Equation 1. The constant a and exponent n will vary for different formulations of propellant.

4.2 Burning Rate Uncertainty

As with any experiment, there is a certain level of uncertainty associated with the measurements made and several precautions have been taken to minimize the

uncertainty of this experiment. Due to the large number of steps it takes to produce these data and the complex, sensitive nature of the combustion of propellant, the uncertainty in the measurements made by this experiment can come from several places. Several, a minimum of 10, samples are tested for each batch of propellant to determine its burning rate characteristics. Samples are checked for consistent density and steady burning. Pressure traces that exhibit a non-linear pressure increase are suspected of non-steady burning and are not used. Several pressures are retested after producing the first burning curve to validate any new trends. Additionally, propellant batches are repeated to ensure correct mixing when needed.

The uncertainty in the burning rate calculation can be made using the standard root-sum-squared method based on the propagation of error from the sample length measurement and burn time calculation. The uncertainty for the calipers used measure the sample's length is ± 0.00025 in, and the uncertainty in the interpolation of the burn start and end time was found to be ± 0.0321 s. For a burning rate of 0.5 in/s and a sample length of 1 in, the uncertainty was found to be ± 0.0080 in/s or 1.6%. However, due to additional uncertainty in mixing and sample variation, an overall uncertainty of 3 to 5 % is assumed, depending on the propellant formulation.

5. SCALE-UP ADDITIVE INVESTIGATION

As alluded to earlier in this thesis, there can be unseen problems associated with the scale-up of additives as shown by Figure 4, where one variation of the additive produced little if any change in the burning rate of the baseline propellant. To investigate possible differences in the additives due to the changes in the scaled-up processing, two variables in the additive synthesis were isolated by a set of formulations that varied the additive's drying method and whether it was heat treated or not heat treated. The resulting four synthesis methods are shown in Table 1. Each synthesis method was investigated with pure titania and Al-doped titania. This parametric approach resulted in a set of 8 additives.

Table 1. Variations of the additive synthesis methods to investigate scale-up issues.

Synthesis Method	Drying Method	Heat Treating
Method 1	Spray	Yes
Method 2	Roto	Yes
Method 3	Spray	No
Method 4	Roto	No

Each additive was tested in composite propellant consisting of 79.2% monomodal AP, 1% additive, and a HTPB binder cured with isophorone diisocyanate (IPDI). This formula is compared to a baseline propellant consisting of 80% monomodal AP and no additive in an IPDI-cured HTPB binder. Propellant samples were prepared with each additive as detailed earlier in this thesis.

5.1 Results

Samples with 1% undoped titania were tested first. Figure 14 shows the resulting burning rate as a function of test pressure on a log plot for the four additive synthesis methods. The dotted line shows the corresponding 80% AP baseline, which contains no additive. The effect on burning rate for the titania additives doped with 3% aluminum is shown in the same manner in Figure 15. The burning rate for each propellant is fitted to the power curve from Equation 1. Values for a and n for each propellant are given in Table 2.

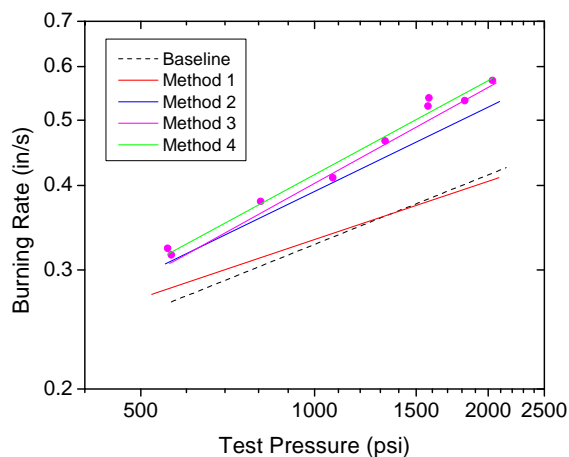


Figure 14. Burning rate as a function of test pressure for propellant with 1% titania for each additive synthesis method. Method 1 (spray-dried and heat-treated) shows no impact on burning rate.

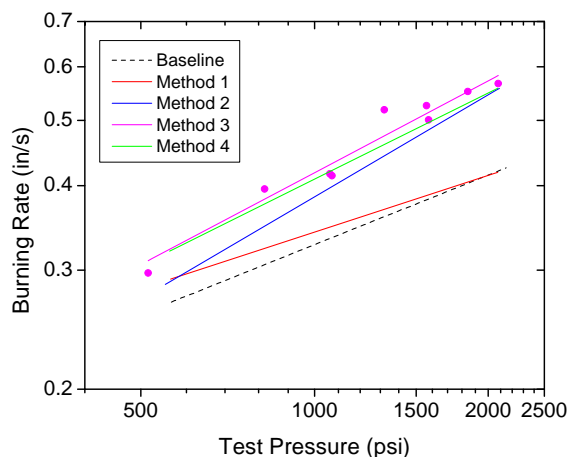


Figure 15. Burning rate as a function of test pressure for propellant with 1% titania doped with 3% aluminum for each additive synthesis method.

In both the pure and Al-doped titania (Figure 14 and Figure 15, respectively), the method used for the scaled-up additives, method 1, showed little increase in burning rate. This effect becomes more evident as the test pressure increases. However, spray drying is not the only parameter causing a negative effect on the ability of the additive to increase the propellant's burning rate. Additives that are not heat treated exhibit a slightly higher burning rate, but a complete loss in effectiveness in the additive is only seen when the additive material is spray dried and then heat treated. Additives that were only spray dried or only heat treated resulted in an increase in burning rate compared to the baseline.

In addition to the pure and Al-doped titania, TiO_2 doped with 3% iron was investigated to confirm the above results. Propellant samples were created using methods 1 and 3 and were tested as before. The results of the strand-bomb testing are

shown in the log plot in Figure 16. The same 80% AP baseline is shown by the dotted line.

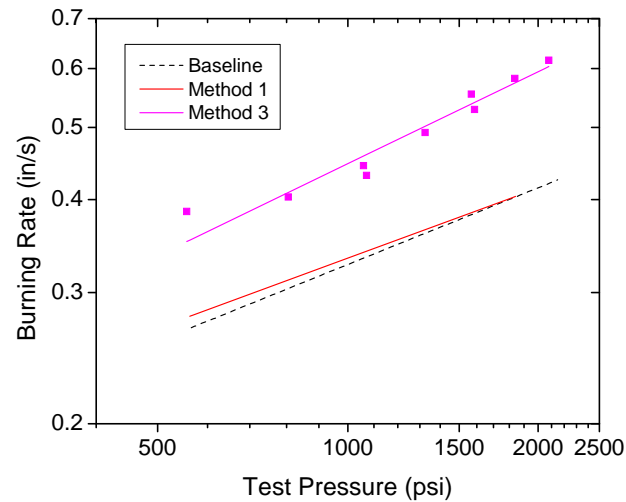


Figure 16. Burning rate as a function of test pressure for propellant containing titania additives doped with 3% iron.

Identical results as seen with the pure and Al-doped titania are likewise seen in the Fe-doped titania, i.e., the additives that are both spray dried and heat treated show no ability to alter the propellant's burning rate. When the additives are not heat treated after being spray dried, they are able to effectively increase burning rate.

Table 2. Values for a and n in the burning rate equation (Equation 1) for each propellant tested in this study. Pressure, P, is in units of MPa, and burning rate, r, is in units of mm/s.

		a	n
-	Baseline	4.29	0.3425
Pure	Method 1	4.85	0.2874
	Method 2	4.47	0.4151
	Method 3	4.11	0.4724
	Method 4	4.31	0.4631
Al-doped	Method 1	5.06	0.2793
	Method 2	3.71	0.5017
	Method 3	4.44	0.4517
	Method 4	4.58	0.4243
Fe-doped	Method 1	4.64	0.3124
	Method 3	5.14	0.4103

In summary, these results show the effect synthesis method has on titania additives' ability to modify the burning rate of composite propellant. Changes in titania's drying and heat-treating produced both effective and ineffective additives. Some titania additives increase burning rate, as previous work showed (Stephens et al., 2010), while the other titania additives had little effect on burning rate, producing results similar to those described in other studies (Ramamurthy and Shrotri, 1996) (Pearson, 1971).

5.2 Discussion

Within the same study are several methods for producing titania additives for composite propellant that produce varying burning rate results, not unlike similar discrepancies seen in past studies. Small differences in the additive's synthesis may have gone unknown in other studies and, as shown in this study, can be the difference between an effective and ineffective burning rate modifier.

To determine which synthesis method is ideal and to develop a theory for the fundamental reason for the differences in batch production, several parameters must be examined. In terms of which additive produced an increase in burning rate, methods 2, 3 and 4 showed the ability to catalyze the reaction and produce an increase in burning rate, with the non-heat-treated additives performing slightly better. As discussed above, the additives that are spray dried have several scale-up and production benefits. The consistent spherical shape of the additive's agglomerates can be seen in SEM images. A comparison of the two non-heat-treated additives is shown in the SEM images of Figure 17 and Figure 18. This comparison leaves one ideal synthesis method; additives produced by spray drying and not heat treated, method 3, were determined to be ideal for the purposes of the authors' current propellant research.

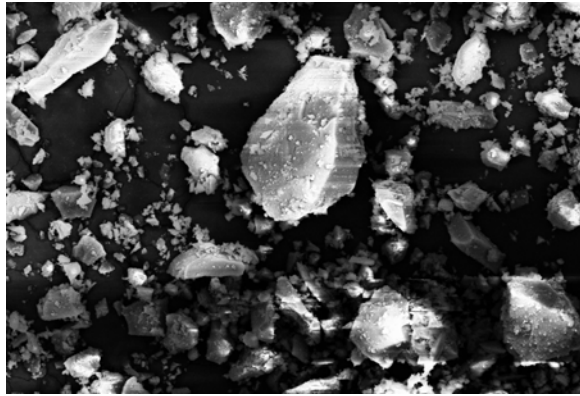


Figure 17. SEM image of non-heat-treated, rotovapped titania that shows the non-uniform shape and wide size distribution of the additive agglomerates.

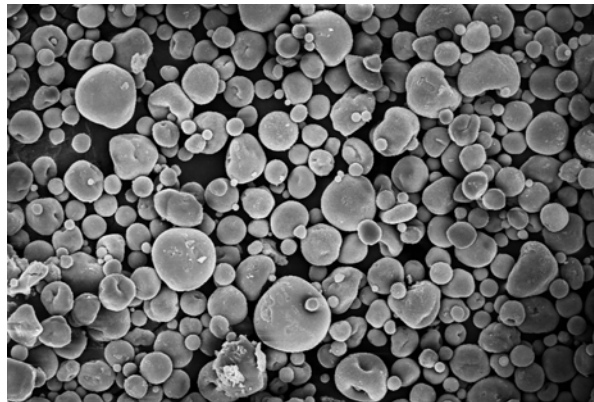


Figure 18. SEM image of non-heat-treated, spray-dried titania that shows the consistent spherical geometry of the agglomerates.

The remaining question is what chemical or physical mechanism is driving this difference in burning rate? One mechanism that at first might seem most likely is that the crystalline structure of the titania is different between synthesis methods that produced an effective additive and those that did not. It is well known how heat treating can affect the crystal phase of titanium oxide (Su et al. 2004), and it has been shown

outside the realm of propellant reactions that the crystal structure of titania can affect its catalytic activity (Andersson et al., 2002). For this consideration, X-Ray diffraction (XRD) tests were performed on each additive. The major crystal phase for each additive was anatase. There is a crystallite size increase after heat treating, from about 5 nm before to 7 nm after, and prior to heat treating there is a very small amount of amorphous content and after there is none. These changes were observed with both the rotovapped and spray-dried additives, yet heat treatment was only detrimental with the spray-dried additives. It is a combination of the drying method and heat treating that produced an ineffective additive, which makes the theory that heat treating is affecting the crystalline structure as the driving mechanism unlikely. With little difference in structure (comparing Figure 5 and Figure 18) and surface chemistry, it is believed the driving mechanism is in the physical properties of the additives when mixed into the propellant.

One possible mechanism to explain the differences in additive effectiveness when mixed with the propellant is that the synthesis method is affecting the physical properties of the additive agglomerates. Additives produced by different combinations of drying and heat treating may have different agglomeration hardness or porosity, and this characteristic could cause the additive to be dispersed in the propellant differently during mixing. In this case, the synthesis method ultimately hinders how the additives are introduced to the reaction zones, resulting in a change in burning rate.

Only reactions taking place in the presence of the catalyst will show an increase in burning rate. Therefore there is some fraction of the reacting propellant which is catalyzed, f_c and some fraction that is not catalyzed $1-f_c$. Only the catalyzed fraction of

the reactions will show an increase in reaction speed causing more heat to be transferred into the propellant and increase burning rate as discussed above. An additive that is poorly dispersed will have a much lower f_c . To investigate this theory, more SEM images were used to compare both backscattering images of cross-sections and images of individual agglomerates. According to this theory it is the production of the agglomerate and the transportation of the additive to the propellant that is hindering the catalytic ability of the additive, not merely the particle size.

There are some difficulties in taking SEM images of additives in solid propellant, namely distinguishing the difference between AP particles and additives. When using the back-scattering detector, the images are produced based on atomic weight and since AP and titania have similar atomic weights they appear similar. However, to investigate the dispersion of the additives the AP crystals are not needed. Additives are mixed into the propellant binder, at 3% by weight, by the same method as making propellant and then cured. This method for producing a binder/additive mixture is assumed to break up the additive agglomerates the same way as mixing actual propellant. Figure 19 shows an image of the spray-dried, non-heat-treated additives in cured binder, and Figure 20 shows an SEM image of the spray-dried, heat-treated additives.

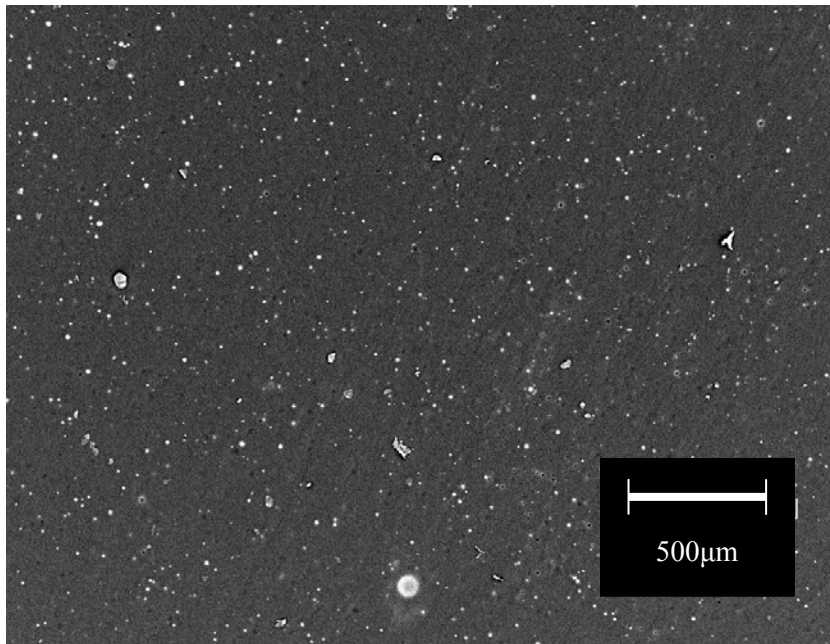


Figure 19. Backscattering SEM cross section image of spray-dried, non-heat-treated titania additives well dispersed in cured binder.

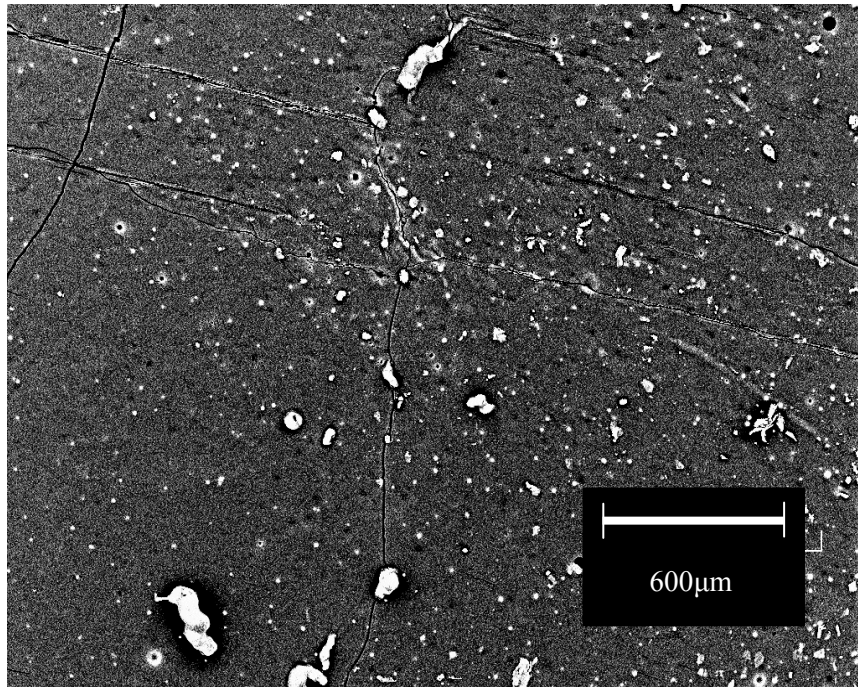


Figure 20. Backscattering SEM cross section image of spray-dried, heat-treated titania additives with large agglomerates after mixing in binder.

Comparing the SEM cross section images of the heat-treated to the non-heat-treated spray-dried additives, there are much larger agglomerates in the heat-treated additives. In addition to having larger agglomerates, the heat-treated additives have a significantly larger number of undispersed or unbroken additive agglomerates. It may appear the non-heat-treated additives in Figure 19 have less additive mass than the spray-dried additives in Figure 20, but this effect is likely due to the better dispersion of the particles which are smaller and cannot be seen in magnification of this type of image.

It is believed by the author that the reason for this physical difference in the additives is caused by sintering that occurs during heat-treating. Sintering causes the particles to fuse together, making them much less likely to break up during mixing.

However the crushing process used in synthesis method 2 would break up a majority of the sintered agglomerates created during heat-treating, but as seen in the burning rate plots (Figure 14 and Figure 15), it is possible some of the sintered agglomerates remained after crushing in method 2 since method 4 had consistently higher burning rate than method 2. This trend is especially notable in Figure 15, which shows the two non-heat-treated synthesis methods are higher than method 2. Figure 21 shows a close up of two different heat-treated additive agglomerates in which the presence of sintering is evident and caused the agglomerate to become smooth and seemingly one particle. Several agglomerates similar to those in Figure 21 were located throughout the propellant with the heat-treated additives. Figure 22 shows a close up of two of the few large agglomerations of the non-heat-treated additives remaining after mixing. The agglomerates in Figure 22 appear to be loosely held together and are distinct particles that do not contain a continuous, smooth surface.

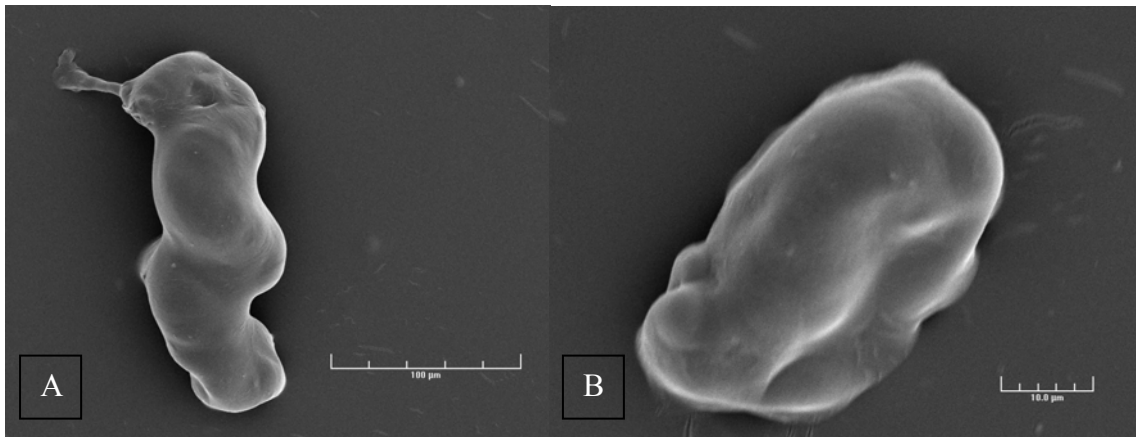


Figure 21. SEM of spray-dried, heat-treated additive agglomerates that have seemingly undergone sintering in the heat treating process making them difficult to break up and disperse when mixed.

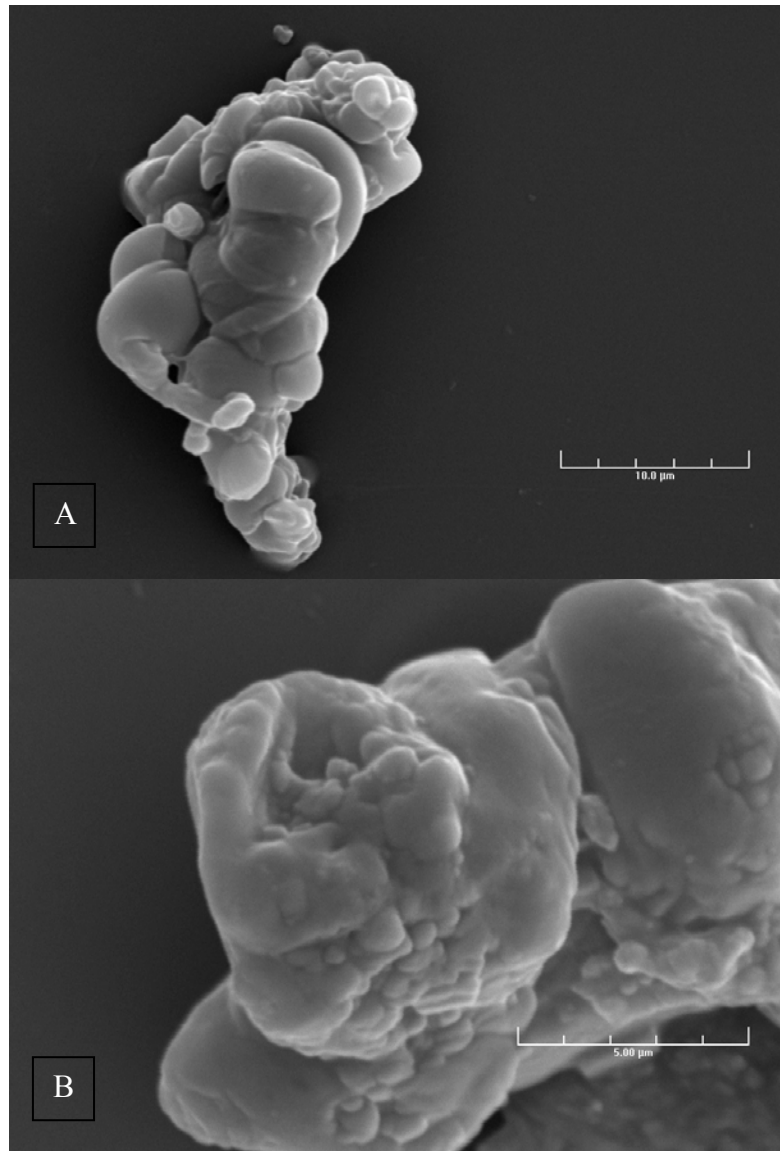


Figure 22. SEM images of non-heat-treated, spray-dried additive agglomerates that have seemingly not sintered and will break apart during mixing.

There are several possible mechanisms at work here, and this complicated topic will require further investigation. Currently it is the author's belief that it is a physical mechanism in the additive agglomerates, as opposed to a chemical mechanism, that

caused the stark difference between the effectiveness of additives that one would otherwise think would perform identically. In summary, there is much to be gained from the results herein when scaling up the production of nanoparticles for motor-sized batches; care must be taken when finalizing the synthesis method since seemingly minor changes in the production method can be the difference between an effective additive and one that does not work at all.

6. ADDITIVES IN MULTIMODAL PROPELLANT

As discussed above there are many properties of the oxidizer crystal AP that affect the burning rate of a propellant. It is possible these sensitivities can also affect how well an additive performs. An initial study into the sensitivity of various propellant parameters on additive performance was conducted by Stephens et al. (2010) and showed both AP percentage and distribution to highly affect how well an additive performs. The propellant formulations for various applications will vary, and for the scale-up tests conducted on these titania additives would be no different. The scale-up propellant formulation would vary slightly from the laboratory propellant the in which the additives were verified. The new scale-up propellant would be 85% bimodal AP propellant with a binder consisting of 2% dioctyl adipate (DOA) plasticizer, 0.3% HX-752 bonding agent, and IPDI-cured HTPB at a cure ratio of 0.82. The bimodal AP consisted of a blend of 30%, 23-micron AP and 70%, 200-micron AP. The baseline laboratory propellant as stated above was an 80%, 200-micron, monomodal AP with IPDI-cured HTPB binder and contained no plasticizer or bonding agents.

The scale-up propellant was prepared and tested as discussed above with 1% pure titania spray-dried additive. As expected, the same additive did not perform the same in the two different propellants. The burning rate as a function of pressure for the laboratory propellant and scale-up propellant with their respective baselines are shown in Figure 23 and Figure 24, respectively. The additive produces a much greater increase in burning rate in the laboratory propellant than in the scale-up propellant.

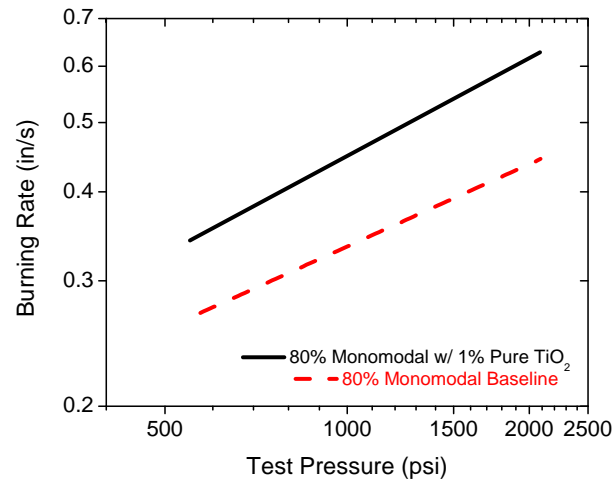


Figure 23. Laboratory propellant containing 80% monomodal AP with 1% pure titania.

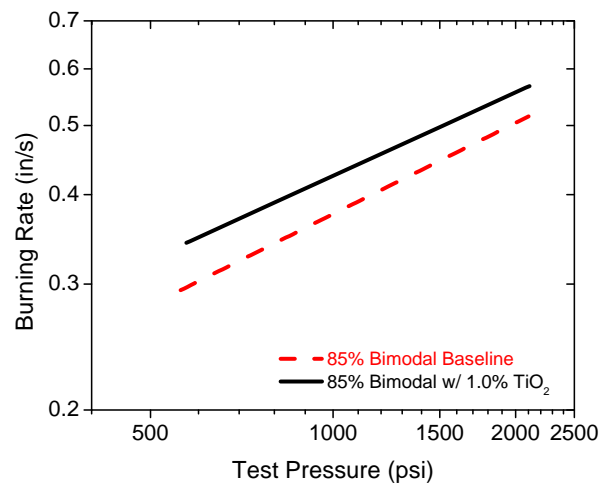


Figure 24. Scale-up propellant containing 85% bimodal AP with 1% pure titania.

6.1 Parametric Study

To investigate the different level of additive effectiveness seen in the two propellant formulations, a parametric study varying the propellant formulations was

conducted. Two variables were isolated, the percentage of AP and the AP size distribution, which produced 4 propellant formulations as shown in Table 3. This study will determine whether the additives are more sensitive to the percent AP or the distribution of the AP that caused scale-up propellant to show a smaller increase in burning rate due to the additive. Each formulation contained 2% DOA, 0.3% HX-752 and 1% pure TiO₂ spray-dried non-heat-treated powder. The four propellants and their corresponding baselines were produced and tested at various pressures as discussed in previous sections of this thesis.

Table 3. Parametric study varying AP loading and distribution.

Propellant Mixture	AP Loading	AP Distribution
1	85%	Bimodal
2	85%	Monomodal
3	80%	Bimodal
4	80%	Monomodal

6.2 Results

The burning rate as a function of pressure according to Equation 1 for the four propellant mixtures can be found in Figure 25 to Figure 28. Each plot shows the propellant containing 1% pure titania and a baseline for the same propellant mixture without additive.

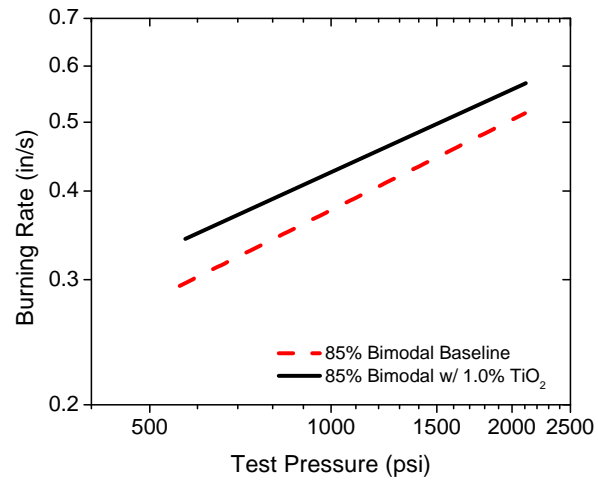


Figure 25. Propellant 1: 85% bimodal AP. The catalyzed propellant showed a 12.7% average increase in burning rate compared to the baseline over the tested pressure range.

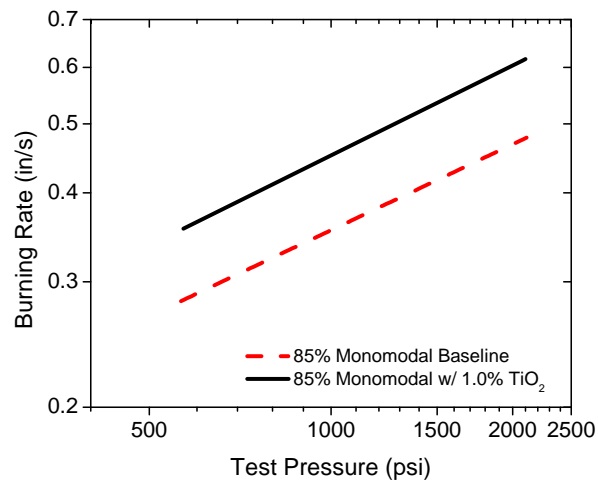


Figure 26. Propellant 2: 85% monomodal AP. The catalyzed propellant produced a 27.7% average increase in burning rate compared to the baseline over the tested pressure range.

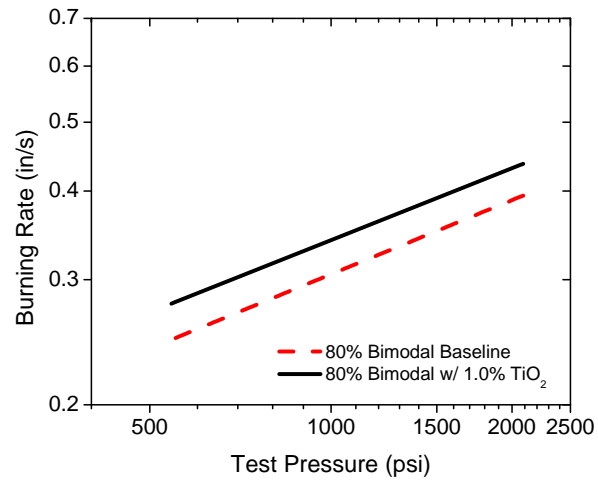


Figure 27. Propellant 3: 80% bimodal AP. The catalyzed propellant produced an 11.3% average increase in burning rate compared to the baseline over the tested pressure range.

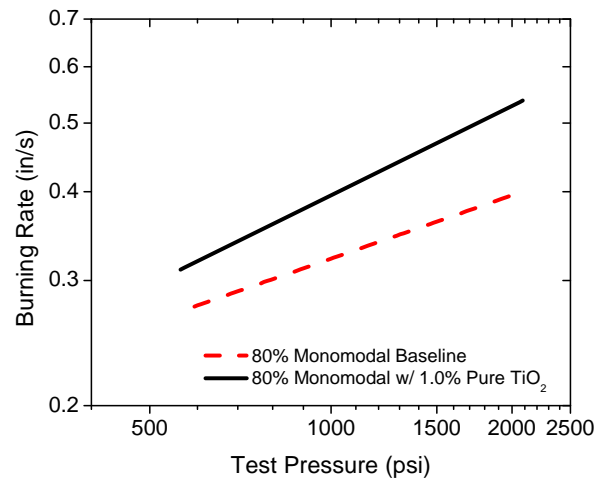


Figure 28. Propellant 4: 80% monomodal AP. The catalyzed propellant produced a 25.2% average increase in burning rate compared to the baseline over the tested pressure range.

6.3 Discussion

Both monomodal propellants showed an increase over the baseline, 25.2% for 80% AP and 27.7% for 85% AP, that are comparable to the increases seen previously by this additive and performed as expected. However, the bimodal propellants showed increases of only 11.3% for 80% AP and 12.7% for 85% AP, which are less than half the increases seen in the monomodal propellants. The additives are slightly more effective in the 85% AP propellants, but the additives are much more sensitive to AP distribution and effective in the monomodal propellants.

The proposed mechanism for this difference in effectiveness is related to distribution, similar to the driving mechanism in the differences seen in the additive scale-up investigation. However the problem is more complex than the agglomeration size of the additive determining the distribution and ultimately the effectiveness of the additive as a burning rate modifier. As discussed above, the additive is only as effective as the number of reactions between the AP and binder it is able to catalyze, which is f_c , the fraction of reaction catalyzed. In the bimodal propellant, 30% of its AP consists of fine AP particles that are 23 microns. These fine AP particles disperse the reactions that the additive attempts to catalyze due to the increase in diffusion area between the AP and binder, ultimately decreasing f_c . The additive is still affecting the same amount of reactions around the coarse AP, as it does in the monomodal propellants, but it is unable to affect all of the reactions around the fine AP, reducing its effectiveness. The introduction of smaller AP particles effectively increases the number of reaction sites that require the presence of the catalyst to perform as expected. f_c and thus the burning

rate depend on a relative dispersion, which is a ratio of the additive dispersion over the dispersion of AP binder reactions, or as stated in Equation 8, for a given amount of additive, f_c is a function of additive agglomerate size over the AP size for each AP size present in the propellant. According to this theory, the additive is less effective in the bimodal propellant only because it contains coarse AP used in the monomodal propellant plus smaller, fine AP. The results would not be the same if the bimodal propellant contained coarse and fine AP, and the monomodal propellant contained only fine AP. In this case, according to the theory presented, the monomodal propellant would show less increase in burning rate than the bimodal propellant.

$$r \sim f_c = 1 - f \left(\frac{D_{Agg}}{D_{AP}} \right)_i \quad (8)$$

To maximize f_c and the effectiveness of the additives, the larger AP can be used; however this apparent solution is not favorable due to a decrease in burning rate and requires a modification to the baseline propellant or the additive can be better dispersed. Better dispersion of the additive will result in more reaction sites being catalyzed and a higher burning rate. There is a limit to the increase in burning rate gained by increasing the dispersion of the additive, and that limit is determined by the AP particle size. After this dispersion limit, additional additive dispersion would produce little to no increase in burning rate. Maximum additive performance would be achieved at this limit and would be ideal for additive use. The limit will be reached sooner with larger AP particles, but as finer AP is used to achieve higher burning rate, a better dispersion will be needed to reach this ideal limit.

7. NEW ADDITIVE INCORPORATION METHOD

Problems with applications of nanoparticle additives have become of particular notice in the solid propellant community. Tingming et al. (2009) stated, “Nanometer metal oxides were highly desirable to increase the burning rate of composite solid propellant because of their high catalytic activities. However, poor dispersibility limits their wide applications.” Tingming et al. are currently working with similar problems to those reported in this thesis and attempting to modify additive production methods of CuO with silica to increase dispersion. The current research at Texas A&M and UCF has also produced a new method for increasing dispersion of additives within the grain of composite solid propellant.

Additives produced with the Sol-gel method have a small particle size, but due to limitations in the preparation and mixing, the advantages gained by the small particle size can be lost in agglomeration, which can lead to poor dispersion and a less effective additive. Work continues to improve the dispersion of additives within composite solid propellant and determine propellant preparation methods that allow for more effective additives. One of the new methods for improved dispersion produces an ultra-fine suspension of additives in the HTPB before the HTPB is added to the propellant. The additive is produced by the sol-gel reaction in a liquid suspension, which is then mixed with HTPB. Then the solvent is removed, leaving an ultra-fine additive suspension in HTPB. The HTPB/additive suspension is then used to create the binder of the propellant. Since the additive does not need to be stored in a powder form, this method significantly

reduces the agglomeration of the additive material, and the agglomerates produced are much smaller compared to other methods.

7.1 Results

This new method of suspending additives in HTPB was first tested with the laboratory propellant formulation. A propellant containing 79.2% monomodal AP and 1.0% Fe-doped titania was produced as before with the exception of using the ultra-fine suspension of the additive in HTPB. The additive was synthesized and suspended in the HTPB at the proper ratio for the specific propellant formulation. Samples were tested as described above at varying pressure from 500 to 2000 psi. Figure 29 shows the burning rate results of the ultra-fine additive suspension, the same formulation using the spray-dried powder, and the corresponding baseline propellant. The 1.0% Fe-TiO₂ spray-dried powder shown in Figure 29 is the highest-performing powder additives for this propellant formulation to date.

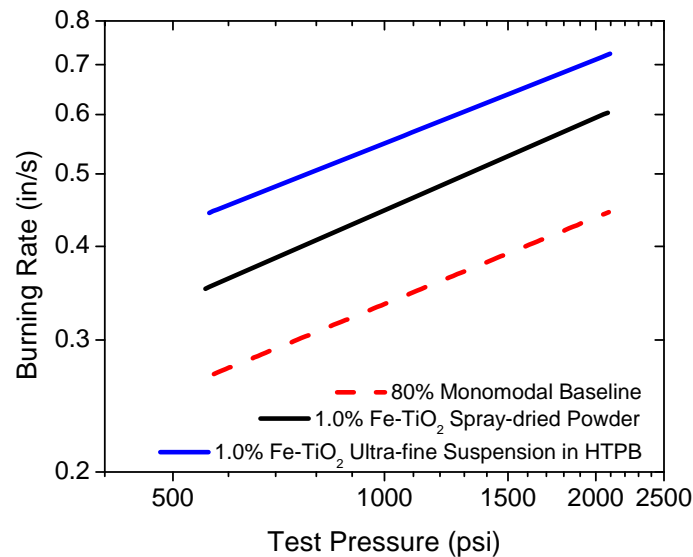


Figure 29. Burning rates as a function of pressure for the new ultra-fine HTPB suspension additives, spray-dried additives of the same formulation and the corresponding baseline.

The propellant containing the ultra-fine suspension of Fe-doped titania in HTPB produced a burning rate which was an average of 62.8% higher than the baseline propellant. The best-performing powder additive, as shown in Figure 29, produced an increase of 34.4% average increase in burning rate over the baseline in the pressures region tested. In the same propellant formulation with the same additive type and percentage, the new method produced a much better dispersion and therefore a much higher burning rate.

Additionally, the new ultra-fine suspension method was tested in the scale-up propellant, which is seen in Figure 24. Recall that additives have not been able to increase the propellant's burning rate to the same extent in this scale-up formulation as other propellant formulations (see Section 6). Propellant consisting of 85% bimodal AP, 2% DOA, 0.3% HX-752, with 0.5% Cu-doped titania suspended in HTPB was produced as stated above. The bimodal AP consisted of 70%, 200-micron and 30%, 23-micron particles, which is the same bimodal mix as before. Initially, an additive loading of 1.0% was tested, but during mixing the propellant binder became too dry and did not produce testable, quality samples, so the propellant was produced with only 0.5% additive. Figure 30 shows the burning rate as a function of pressure for the 85% bimodal AP propellant with 0.5% Cu-doped titania ultra-fine suspension in HTPB, the burning rate for 85% bimodal AP propellant with 1.0% pure titania spray-dried powder, and the corresponding baseline.

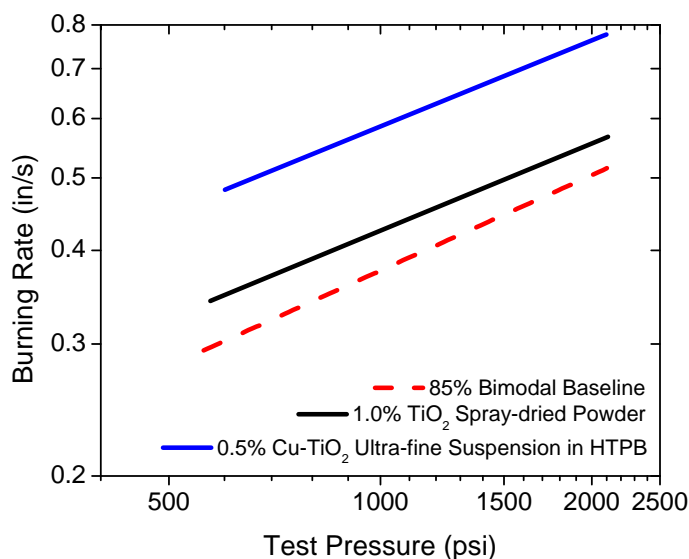


Figure 30. Burning rate as a function of pressure for the 85% bimodal AP propellants containing 0.5% Cu-TiO₂ ultra-fine suspension in HTPB, 1.0% TiO₂ spray-dried powder and baseline.

The 85% bimodal AP propellant containing 0.5% ultra-fine suspended additive in HTPB produced a 53.4% average increase in burning rate over the baseline propellant. The same formulation containing 1.0% spray-dried titania powder previously showed an average increase of only 12.7%. Even at half the mass loading of the spray-dried additive, the ultra-fine suspended additive in HTPB performed extremely higher due to its better additive dispersion. The new additive incorporation has alleviated the problematic performance of powder additives in bimodal propellants containing fine AP.

The improved method for incorporating additives into composite solid propellant takes advantage of smaller agglomerate size to improve dispersion. This new method

follows the proposed theory of relative dispersion as the driving mechanism for the improved effectiveness of the additives. The better dispersion leads to more reactions being catalyzed and a higher burning rate, but as smaller AP is used the reactions become more finely dispersed allowing more reactions to take place without a catalyst. This smaller AP then results in a less effective additive, but with adequate dispersion, as in the ultra-fine suspension, this loss in effectiveness can be overcome.

The dispersion of the ultra-fine additive suspension can be seen in Figure 31 using the same method of backscattering SEM imaging as in Figure 19 and Figure 20. It appears there is less additive in Figure 31, but this illusion is due to the reduced agglomeration size. Upon closer examination of the image, fine detections of additives can be seen between the larger agglomerates. Also, based on the scale of the image and the amount of additive seen in other images of the same quantity of additive, there is additive too small to be seen in this type of image. Images taken at higher magnification show a few large agglomerates of 2 to 3 microns, but a majority of the agglomerates are less than a micron in size. A sample of some of these images can be seen in Figure 32.

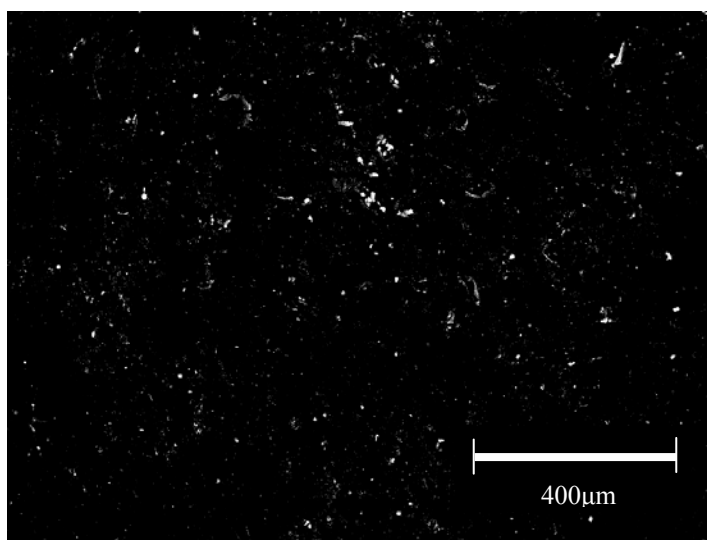


Figure 31. Backscattering SEM cross section image of the ultra-fine suspension additive in cured HTPB.

The new additive incorporation method of ultra-fine suspended additives in HTPB produces not only a higher burning rate but also effective bimodal propellants containing fine AP. According to the theories presented in this thesis, these improvements result from an improved relative dispersion of the additive material and the catalyzed reactions. These results are another example of complex sensitivities associated with the application of nanoparticle additives in composite solid propellant. As reported, this catalytic additive and method increased the burning rate of the propellant by 53.4%, which are excellent results when compared to other reported catalysts. Recently, the work by Tingming et al. (2009) reported a new method for CuO additive preparation that produced an increase in burning rate of 9.5%.

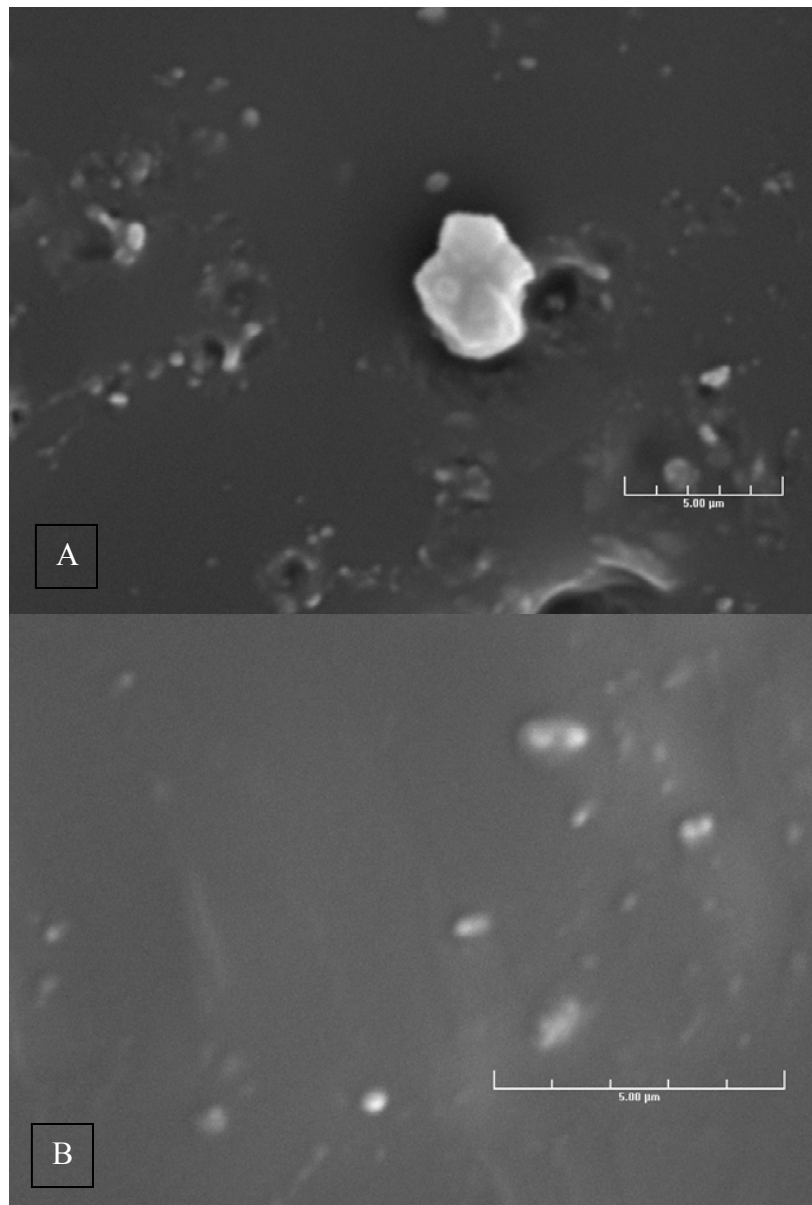


Figure 32. SEM image of one of the few large agglomerates (A) and a sample of the average agglomerate size (B) of the ultra-fine suspension of additive in HTPB.

8. CONCLUSIONS

In the current studies, titania has been seen to be both an effective and ineffective burning rate modifier when used as an additive in AP/HTPB composite propellant with numerous parameters influencing its effectiveness. Differences in manufacturing method were required to produce large amounts of additive for use in separate rocket motor experiments. The additive synthesis method when scaled up influenced how effective the additive was at increasing burning rate. Nano titania that is spray dried and then heat treated was shown by several propellant batches to produce an ineffective additive. The ideal synthesis method was found to be spray drying without heat treating. This procedure produced an effective burning rate modifier in powder form while retaining the benefits of spray drying. The theory is that the difference is not caused by chemical differences in the final additives but is instead caused by physical differences in the additive agglomerates. The agglomerates were unable to break-up in the mixing process and were not well dispersed in the propellant grain. Based on SEM images, the heat-treating process was shown to sinter the particles together causing them to fuse into a hardened agglomerate. Ultimately this particle fusion limited the number of reactions the additive could catalyze during the burning process and made the additive ineffective.

The current additives were studied in various propellant formulations including monomodal and bimodal propellants and different AP loading levels. It was found that the spray-dried titania additives were more sensitive to AP distribution than AP loading level. The additives were more effective in monomodal propellant than in bimodal

propellant for the tests conducted. However, it was determined this was due to the bimodal propellant containing fine AP, which disperses the reactions that the additive attempts to catalyze to increase burning rate. The effectiveness of the additive was shown to be related to the additive's relative dispersion, which is a ratio of the additive dispersion to the dispersion of the AP-binder reactions created by the smaller AP.

A new method for incorporating the titania additives into the solid propellant matrix was created to improve the dispersion of the additives, which according to the previous results should create a much more effective additive in propellants with smaller AP such as the bimodal formulation used in the previous study. The new method consisted of suspending ultra-fine titania additive in HTPB and using the additive suspended HTPB to create the binder. Propellant created with the new additive dispersion method showed a significantly higher burning rate in both monomodal AP propellants and bimodal propellants containing fine AP. The ultra-fine suspension of additive in HTPB was able to modify the burning rate of the bimodal propellant that the spray-dried powder was unable to modify. The results from the new additive incorporation method agreed with the theory of relative dispersion proposed in this thesis.

The results presented in this thesis were for titanium dioxide nanoparticles produced by the sol-gel method, but the underlying concepts of additive processing, scale-up, incorporation, and dispersion apply to a variety of nanoparticles, especially those created by the sol-gel reaction. Problems with agglomeration and scale-up are typical for the application of nanoparticle additives and their use in composite propellant

is no exception. The large quantities of additives and the environment for producing an actual solid propellant motor add to the complexities and problems facing the application of nanoparticle burning rate modifiers in composite propellants. It is difficult to take additive results directly from laboratory experiments such as TGA tests and implement them directly into working propellant formulations. This work attempts to bridge the gap between those laboratory experiments and full-scale composite solid propellant motors using nanoparticle additives as a catalytic burning rate modifier.

9. RECOMMENDATIONS

After several decades of research into solid propellant, there are many unknowns remaining. Effects of specific additives are known but with numerous parameters associated with each additive, there is a need to understand the underlying fundamental concepts. Detailed empirical studies, such as those presented in this thesis, are a necessary stepping stone towards the goal of developing purely theoretical predictions of additive performance. Much work in both empirical testing and theoretical modeling of both propellant and additives exist between our current knowledge and this long term goal.

In addition to long term goals, there are several investigations that can help validate the theories presented in this thesis, some of which has already begun at TAMU. The author would recommend testing the limits of relative dispersion by testing additives of various dispersion in very fine and very coarse AP propellants. Possibly with this information it would be possible to correlate a function for relative dispersion. Additionally, more work developing different imaging techniques with the SEM is needed to better quantify the dispersion of additives within a propellant grain. It may be possible to make additives easier to detect using alternative or new additive doping materials.

Additionally, there are many studies of numerous additives and AP in TGA tests, but many of these tests lack detail burning rate, additive dispersion, and processing investigations. These detailed tested are needed to fully understand these potential

burning rate modifiers. Once good additives are identified, it will be necessary to determine the ideal method for producing the additive. It is recommended that various methods for producing titanium other than the sol-gel method are investigated to examine possible differences in additive performance.

Finally, additional work in coupling detailed kinetics and three-dimensional mass transport modeling is needed to fully model combustion of solid propellant. Then incorporate the catalytic activity of the additives into the kinetics model.

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