

Comparison of Commercially Available and Synthesized Titania Nano-Additives on the Burning Rate of Composite HTPB/AP Propellant Samples

A. R. Demko,¹ T. W. Allen,¹ M. Johnson,¹ D. L. Reid,² S. Seal,²
and E. L. Petersen¹

Texas A&M University¹
College Station, Texas, USA

University of Central Florida²
Orlando, Florida, USA

Key words: AP, HTPB, monomodal, bimodal, titania

1 Introduction

Tailoring the performance of composite solid propellants relies on the use of various additives and additive sizes. While solid propellants are formed using a majority of binder, fuel, oxidizer, and curative by mass, additives are introduced, in relatively small quantities, to augment distinct parameters of the propellant. Different additives improve individual aspects of the propellant such as shelf-life, elasticity, and combustion performance [1, 2]. With the rise of interest in nano-scale technologies, combustion research has found interest in nano-sized additives to enhance the burning performance of propellants. Additives are produced both commercially and in a laboratory setting for further research in combustion. The reduction in the particle size enhances the combustion reaction by several distinct mechanisms. Reduction in the particle's mass lessens the transient heat conduction travel time through the particle, and an increase in the surface-to-volume ratio yields better dispersion of the particles in the propellant, increasing the reactant sites. Finally, the nano-scale particles can have completely different surface chemistry, often better than their micron-sized counterparts [4-9]. A representation of how the dispersion of the nano-particles varies from the micron catalysts can be found in the work by Stephens et al. [10].

In the desire to control particle composition, prevent agglomerations, increase dispersion of the particles, and reduce the size of the particles, nano-additives are manufactured in the authors' laboratory using sol-gel methods. These particles are based on titania and can also be doped with various metals, such as iron. Once the particles are in the sol-gel solution, they are wet mixed and dispersed directly into the HTPB, resulting in particles that are ready to be deployed in solid propellant not dealing with powders helping to prevent agglomerations [11-14]. Mach I® utilizes a wire

explosion method that results in dry powder that tends to agglomerate when dry-mixed into HTPB. This paper summarizes some recent work in our laboratories on the pre-mixing nano-additive methods and compares propellants made using them with propellants manufactured with off-the-shelf titania nanoparticles. Presented first are details of the experiment, followed by the results that compare the two types of catalysts and mixing techniques.

2 Experiment

A series of experiments were conducted comparing the use of commercial titanium dioxide (titania) from Mach I® and the use of laboratory-produced titania from the present authors. The propellant formula consists of hydroxyl-terminated polybutadiene (HTPB), ammonium perchlorate (AP), and isophorone diisocyanate (IPDI). Propellants were mixed based on both 80/20 and 85/15 AP/HTPB mass ratios, with various mass loadings of titania, both Mach I® and laboratory nano-particles made with the same percentages. Pure-AP/HTPB propellants (i.e., without a metal fuel such as aluminum) were utilized in the present study for several reasons, primarily to isolate the catalytic additive effect, which is thought to act on the oxidizer burning process; and, also because such non-metalized propellants are of interest for certain applications. For similar reasons, propellants with and without fine AP particles were made so that the effect of AP distribution on the effectiveness of the catalyst could be examined as well.

All propellant was produced by hand-mixing techniques developed in 20-gram batches to ensure an adequate number of testing samples and so the propellants were uniformly mixed. The approximate size of the coarse AP particles was 200 µm, and the fine AP was 20 µm used in the bimodal mixtures. A binder of R-45M HTPB from Aerocon Systems was cured by IPDI. Thorough explanation of the mixing method is explained and validated by Stephens et al. [15]. For the particles manufactured by the authors, they were pre-mixed into the HTPB as soon as they were produced to minimize the agglomeration of the additive. For the mixtures containing the commercially available additive, the powdered additive was mixed into the propellant during the mixing stage, in the usual fashion when preparing propellants from separate ingredients from separate suppliers.

A minimum of ten propellant strands were tested at 25-mm lengths in the laboratory strand burner, discussed in more detail in Stephens et al. [7]. Samples were tested in an inert gas, argon, at incremental pressures beginning at 3.44 MPa and incremented to 13.8 MPa. As the pressure changes with time, the data were recorded and analyzed to find the burning rate and the percent increase in pressure using pressure transducers connected to a GageScope data collection board using software from Gage Applied Sciences. Batches using both additives were made at the same mass percentages, using additives that were 0.5-1.0% by mass of the overall propellant formulation. From the burning data, the burning rates were compared to verify if the performance enhanced.

3 Results

Once the burning rate data were collected for the described pressure range, data from the individual propellant batches were plotted on a single graph to produce the characteristic function of the burning rate as a function of pressure. Since the relationship of the burning rate is exponential, a conversion to a logarithmic scale is utilized to produce a linear relation. Traditionally, the burning rate is expressed as a function of pressure in the following equation [2]:

$$r = a P^n$$

Where r is the burning rate, a is the leading coefficient, P is the chamber pressure, and n is the pressure exponent. The leading coefficient is indicative of the burning rate's magnitude and is often referred to as the temperature coefficient, and it is found to be altered based on the initial temperature of the

propellant strand. All tests were conducted under a constant temperature of 21° C to eliminate a fluctuation in the magnitude of the burn data.

In Fig. 1 on the left, a standard baseline propellant at 80% AP is compared to an 85% AP bimodal propellant (i.e., propellant containing both 200-micron and 20-micron AP). It can be observed that the propellant containing the higher amount of AP will have a higher burning rate, as is well known, and the remaining graphs are compared to the appropriate baseline. Figure 1 (on the right) demonstrates the trends of the 80% AP propellants with 1%, by mass, of Mach I® and laboratory-produced titania. Titania manufactured in the authors' laboratory is seen to have a slightly higher burning rate than that of the commercially available nano-additive. Nonetheless, it is interesting to see that both types of titania additive provide an increase in the propellant burning rate, providing further validation that titania can be considered a useful catalyst for enhancing propellant burning rates. Table 1 shows the information about the propellants tested and the experimental burning rates. Results shown in Fig. 2 are from propellant batches containing 0.3% titania additive, and it should be noted that there is better performance from the laboratory particles at a similar magnitude seen in Fig. 1.

Table 1: Characteristics of some prehistoric films for high speed diagnostic given pressure in MPa

Lab/Mach I	AP%	AP Distribution	% Additive	Average Burning Rate (mm/s)	Burning rate coefficient a	Burning rate coefficient n
Baseline	80	Monomodal	0.0	9.0	4.06	0.38
Baseline	85	Bimodal	0.0	10.0	5.04	0.33
Mach I	85	Bimodal	1.0	21.3	5.97	0.59
Lab	85	Bimodal	1.0	24.2	6.80	0.57
Mach I	80	Monomodal	1.0	15.5	6.10	0.42
Lab	80	Monomodal	1.0	18.9	6.60	0.46
Mach I	80	Monomodal	0.3	12.4	4.52	0.48
Lab	80	Monomodal	0.3	14.3	6.07	0.38

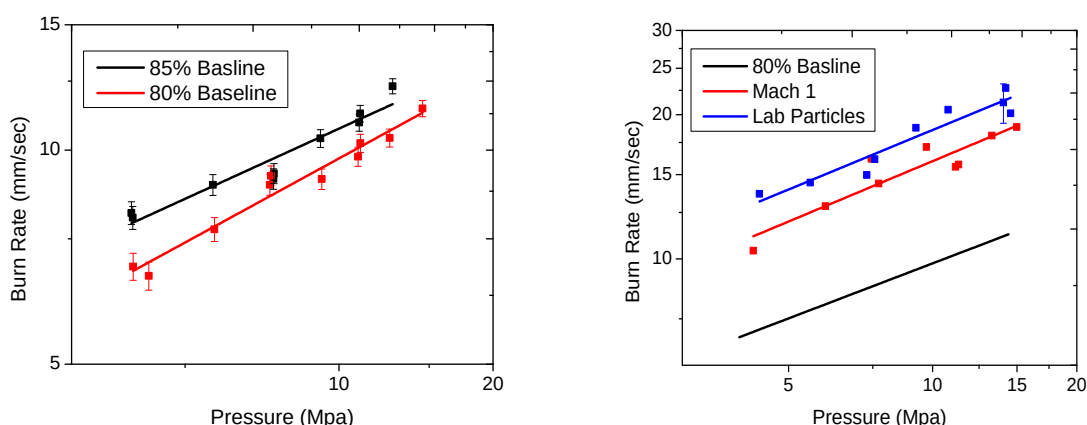


Figure 1: On the left, burning rate plots of 80% monomodal and 85% bimodal baselines. On the right, 80% monomodal mixtures comparing Mach I® and Laboratory-made nano-titania. Additives are 1% by mass.

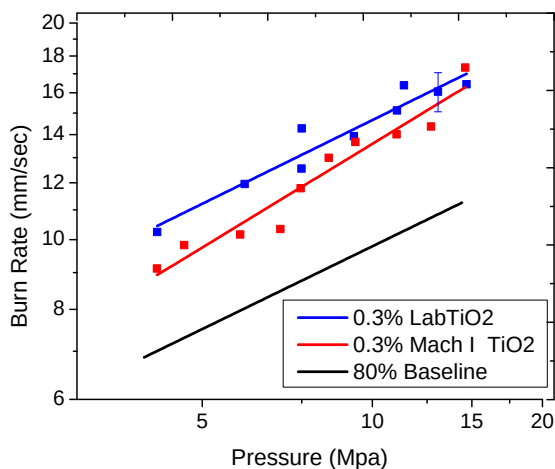


Figure 2: 80% monomodal mixtures comparing Mach I[®] and laboratory-made nano-titania. Additives are 0.3% by mass.

Figure 3 (left) displays the burning rate trend of a typical propellant with the addition of titania by 1% mass to the 85%, bimodal-AP propellant combination. It can be observed that additives made in the authors' lab produce a burning rate that is 20 to 30% faster than what is obtained with the use of Mach I[®] nano-additives. Thus, the titania has relatively the same reduced effect on the bimodal propellant at the higher AP concentration. In Figure 3 (right) the burning rate of 85% bimodal AP distribution with both commercial nano-additive and the laboratory premixed additive, however the mass percent's are different. The laboratory nano-titania is added to the propellant at 0.5% by mass, where the commercial one is at 1.0% by mass and it is observed that the burning rates are approximately equal. Using lower amounts of the laboratory particles produce the same increase in performance as the commercial metal oxide allowing for the use of more additive to increase the propellant performance. Using the premixing method allows for more of an increase in the burning rate for a bimodal mixture.

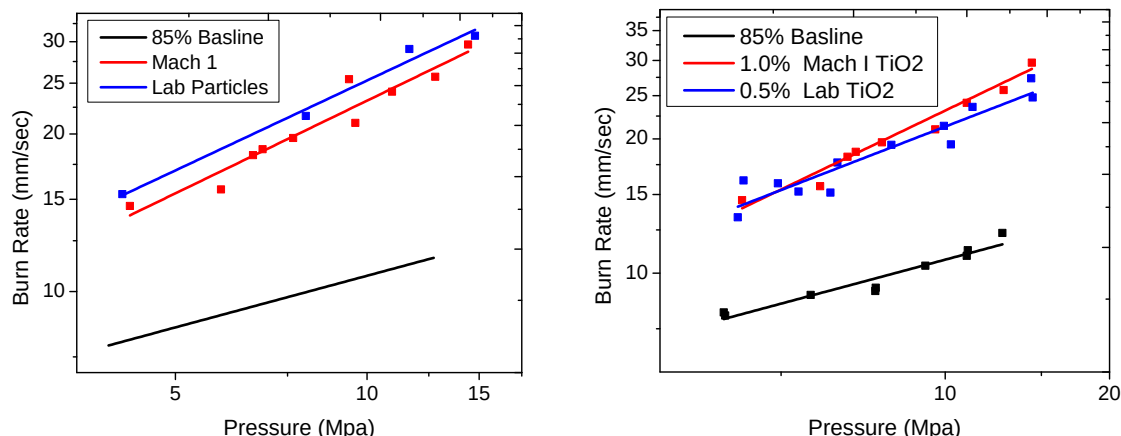


Figure 3: On the left, Propellants at 85% bimodal mixtures comparing Mach 1[®] and Laboratory made nano-titania. Additives are 1% by mass. On the right, Propellants at 85% bimodal mixtures comparing Mach 1[®] and Laboratory made nano-titania. Laboratory premixed additive at 0.5% and Mach 1 dry additive at 1.0% by mass.

4 Analysis

Titania produced in the authors' laboratory is shown to have slightly higher performance than the titania purchased from Mach 1[®]. The reason for the slightly better performance is most likely due to the fact that the particles synthesized in our laboratory were of higher purity and more spherical in shape. Also, the pre-mixed propellant performed better since the particles were mixed into the HTPB immediately after being manufactured, reducing the agglomerations and increasing dispersion. Also, the size distribution of the particles ranged from 5 to 10 nm, while the smallest commercial additive was 20 nm. The smaller nano titania is better distributed in the propellant, thus more efficiently catalyzing combustion of the propellant. An additional increase of approximately 20 to 30% was found for the nano-particles made in authors' laboratory when compared to the commercial additives.

5 Summary

This study compared the use of commercial titania nano-additives with titania nano-additives manufactured in the authors' laboratory. Propellants studied were at 1% additive by mass and both 80% monomodal and 85% bimodal AP distribution to show the fine AP does not influence the additive's performance. Burning rate tests confirmed the enhanced capabilities of the laboratory particles producing burning rates 20-30% faster than its commercial counterpart.

With the new nano-technologies emerging, current methods for producing nano-particles have improved, leading to larger catalytic effects in solid propellants. Manufacturing catalysts in the authors' laboratory allow for a reduction in the size of the metal oxide, which are smaller than what is commercially available. Along with the smaller particles, preventing large amounts of agglomeration is achieved by immediately mixing the nano-additives into HTPB as soon as they were ready. More work is being done to improve the manufacturing of nano-particles to be used as catalysts in solid propellants.

References

- [1] Davenas, A., (2003). Development of Modern Solid Propellants, *Journal of Propulsion and Power*, Vol. 19, No.6, 1108:1128.
- [2] Sutton, G. P., Biblarz, O. (2001) *Rocket Propulsion Elements*, 7th ed., John Wiley, New York. (ISBN 0-471-52938-9).
- [3] Masala, O., Seshadri, R. (2004). Synthesis Routes for Large Volumes of Nanoparticles. *Annual Review of Materials Research*, Vol. 34, 41:82.
- [4] Meda, L., Marra, G., Galfetti, L., Inchingalo, S., Severini, F., De Luca, L., (2005). Nanocomposites for Rocket Solid Propellants, *Composites Science and Technology*, Vol 65, 769:773.
- [5] Blomshield, F. S., Nguyen, S., Matheke, H., Atwood, A., Bui, T. (2004). Acoustic Particle Damping of Propellants Containing Ultra-Fine Aluminum. *AIAA Paper 2004-3722*.
- [6] Dokhan, A., Price, E. W., Seitzman, J. M., and Sigman, R. K. (2002) Combustion Mechanisms of Bimodal and Ultra-Fine Aluminum in AP Solid Propellant, *AIAA Paper 2002-4173*.
- [7] Stephens, M., Carro, G., Wolf, S., Sammet, T., Petersen, E. (2005). Performance of AP-Based Composite Propellant Containing Nanoscale Aluminum. *AIAA Paper 2005-4470*.
- [8] Wang, Y., Zhu, J., Yang, X., Lu, L., and Wang, X. (2005). Preparation of NiO Nanoparticles and their Catalytic Activity in the Thermal Decomposition of Ammonium Perchlorate. *Thermochimica Acta*, Vol. 437, 106:109.
- [9] Egdell, R. G. Jones, F. H. (1998). Structure and reactivity of oxide surfaces: new perspectives from scanning tunneling microscopy. *Journal of Material Chemistry*, Vol 8, 469:484.
- [10] Stephens, M., Petersen, E. (2007). Addition Methods of Nanoscale Additives in Solid Composite Propellants. *AIAA Regional II Student Conference*.
- [11] Krietz, K., Petersen, E., Reid, D., Seal, S., (2011). Relative Dispersion of Catalytic Nanoparticle Additives and AP Particles in Composite Solid Propellant and the Effect on Burning Rate. *AIAA paper 2011-418*.
- [12] Reid, D., Kreitz, K., Stephens, M., King, J., Nachimuthu, P., Petersen, E., Seal, S. (2011). Development of Highly Active Titania-Based Nanoparticles for Energetic Materials. *Journal of Physical Chemistry*. Vol. 115. 10412:10418.
- [13] Stephens, M., Petersen, E., Carro, R., Reid, D., Seal, S. (2010). Multi-Parameter Study of Nanoscale TiO₂ and CeO₂ Additives in Composite AP/HTPB Solid Propellants. *Propellants, Explosives, Pyrotechnics*, Vol. 35. 143:152.
- [14] Reid, D., Kreitz, K., Stephens, M., Petersen, E., Seal, S. (2011). Catalytic Nanoparticle Additives In Composite Solid Propellants With Emphasis On Additive Dispersion And Burning Rate. *JANNAF 2011-1765*.
- [15] Stephens, M., Sammet, T., Carro, R., LePage A., Petersen E. (2007). Comparison of Hand and Mechanically Mixed AP/HTPB solid Composite Propellants, 43rd AIAA joint Propulsion Conference and Exhibit, *AIAA Paper 2007-5765*.