JOURNAL OF PROPULSION AND POWER
Vol. 18, No. 1, January–February 2002

Technical Notes

TECHNICAL NOTES are short manuscripts describing new developments or important results of a preliminary nature. These Notes cannot exceed 6 manuscript pages and 3 figures; a page of text may be substituted for a figure and vice versa. After informal review by the editors, they may be published within a few months of the date of receipt. Style requirements are the same as for regular contributions (see inside back cover).

Anomalous Deflagration Behavior of Ammonium Perchlorate at Elevated Pressures

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

Introduction

THE purpose of this Note is to draw attention to the long known but little recognized or understood "anomalous burning" behavior of ammonium perchlorate (AP), the principal ingredient used in almost all composite solid rocket propellants today. Specifically, the present work highlights some gaps in the literature pertaining to diagnosing such anomalous behavior that have been introduced by disparities in the test methods and the interpretation of observations made with the different test methods.

The deflagration rate of pure AP is known to exhibit a substantial "mesa burning" trend in the 2000–4000 psi (13.8–27.56 MPa) pressure range (see Fig. 1) (Ref. 1). This observation has been reported not only for samples formed out of pure single crystals of AP but also for those made from pressed pellets of particulate AP of high purity.[2, 3] The mesa burning trend is extremely sensitive to the presence of impurities,[1] as has also been supported by experiments performed with single crystals of AP that were isomorphously doped with calculated amounts of relevant impurities.[4] The pressure range noted earlier corresponds to the samples initially being at room temperature. The onset of the mesa burning trend has been shown to shift to higher pressures at higher initial temperatures of the sample (pressed pellets of AP).[5] The mesa burning rate trend is associated with a transition from steady regression to a rather complex mode of deflagration that involves the following unique features: 1) macroscopically irregular surface regression,[1,6] 2) locally intermittent flamelets on the same spatial- and timescales as the irregularities in surface regression, with the flamelets standing above recessed sites,[1,4,6,7] and 3) an extraordinarily complex topochemistry in which locally recessed areas of the overall burning surface consisted of arrays of parallel needles 100–200 μm long, $\sim$5 μm across, with the top of the needle array presenting a pseudosurface (see Figs. 2f and 3f of Ref. 4). The exact physicochemical mechanisms involved in this mode of deflagration, the explanation for the mesa burning rate trend, and interpretation of the corresponding surface features, are still very poorly understood. For this reason, the behavior has come to be termed "anomalous."

The importance of AP self-deflagration behavior in the combustion of composite propellants at elevated pressures cannot be overstated. According to conventional models of propellant combustion (e.g., Ref. 8), the AP self-deflagration flame has a major role in governing the propellant burning rate above $\sim$1000 psi (6.89 MPa). Recent interest in elucidating the mechanisms responsible for plateau burning rate trends of composite propellants with AP has raised the possibility that the mesa burning trend of AP at elevated pressures and the corresponding deflagration behavior may offer a plausible mechanism for observation of plateau burning rates in propellants.[9]

The scope of the present work is very limited insofar as understanding the governing processes in the anomalous burning regime of AP is concerned. In trying to study the relevant literature on the subject, a close inspection of the available observations reveals that sufficient evidence for an exact correspondence between the mesa burning behavior of AP and the occurrence of a complex deflagration pattern is lacking. The situation has been exacerbated by the adoption of two different test methods, that is, methods to interrupt the burning, for examination of the quenched surface of the samples in a scanning electron microscope (SEM). The two methods have been presumed, it appears, to yield identical observations over the entire pressure range of interest, without sufficient evidence that warrants such presumption.

Background

A brief summary of the available observations in the literature is presented to highlight the discrepancies in the interpretation of the results.

Hightower and Price[10] first reported high-speed cinematography of deflagration of single crystals of AP. They also performed quenching by rapid depressurization (referred to in short as dp/dt hereafter)

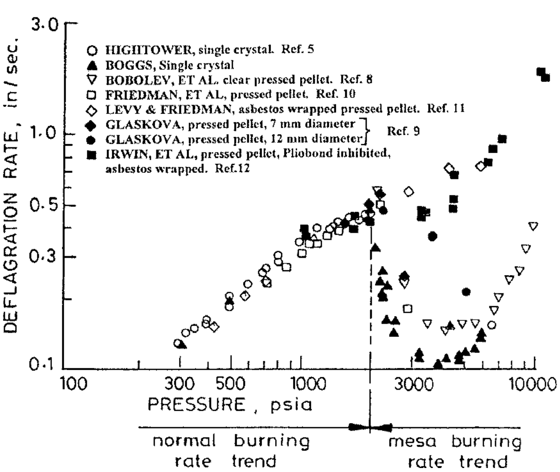


Fig. 1 Self-deflagration rate of AP (taken from Ref. 1).

Received 29 April 2001; revision received 8 July 2001; accepted for publication 13 July 2001.

*Postdoctoral Fellow, School of Aerospace Engineering; currently Assistant Professor, Department of Aerospace Engineering, Indian Institute of Technology, Madras, Chennai 600 036, India. Member AIAA.

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

‡Senior Research Engineer, School of Aerospace Engineering, (retired).

§Graduate Research Assistant, School of Aerospace Engineering; currently Propulsion Research Engineer, Chemical Systems Division, United Technologies, San Jose, CA 95161-9028.

up to 800 psi (5.51 MPa) for examination in an SEM. They reported, based on observations in the photography experiments, that the deflagrating surface of AP had a fingerprint pattern, with the presence of a liquid froth on the deflagrating surface. These observations were corroborated by the remnants of the froth such as burst bubbles that were frozen on the quenched surfaces as seen in the SEM.

Boggs,[1] Boggs et al.,[4] and Boggs and Kraeutle[6] adopted a thermal-quench method as well as the dp/dt-quench method, the former involving deflagration of the sample clamped between two copper blocks that act as heat sinks to drain the heat from the reaction zone, thereby quenching the deflagrating sample. Both quench methods were adopted up to 1200 psi (8.27 MPa); for pressures higher than this level, only the thermal-quench method was adopted. Up to 1200 psi (8.27 MPa), the surface features of AP corresponded to normal deflagration behavior, as Hightower and Price[10] had reported. However, the appearance of uneven regression surfaces with pockets of needle arrays were reported at pressures of 1500 psi (10.34 MPa) and above, based only on thermally quenched samples.

Varney[3] reported surface features based on the dp/dt-quench technique at 1200 psi (8.27 MPa) and 4800 psi (33.08 MPa) of pressed pellets of high-purity AP. The surface features at 1200 psi (8.27 MPa) appeared to correspond to normal deflagration, but the one at 4800 psi (33.08 MPa) indicated sporadic prevalence of sites filled with needlelike structures symptomatic of anomalous burning behavior.

Boggs,[1] Boggs et al.,[4] and Boggs and Kraeutle[6] were careful to compare 1) single-crystal AP vs pressed pellets of high-purity AP and 2) dp/dt-quenched samples vs thermally quenched samples. The equivalence between the behavior of single crystals and pressed pellets was established nearly completely. This is indeed reconfirmed by the new results of the present investigation. However, in attempting to examine the equivalence of the two quench methods, they noted that the two methods yielded similar observations not only up to 1200 psi (8.27 MPa), based on direct comparisons of their results and those of Hightower and Price[10] [upto 800 psi (5.51 MPa)], but also at higher pressures, based on similarities in their results obtained by thermal quenching with those obtained by Varney[3] using the dp/dt-quench method at 1200 (8.27 MPa) and 4800 psi (33.08 MPa).

In the pressure range of 1200–4800 psi (8.27–33.08 MPa), a range that includes the crucial onset of mesa burning rate trend at 2000 psi (13.8 MPa), the only available observations of quenched surfaces are those obtained by thermal quenching of samples, by Boggs,[1] Boggs et al.,[4] and Boggs and Kraeutle.[6] Because these results indicate the occurrence of a nonuniform regression surface with sporadic distribution of pockets of needles at pressures as low as 1500 psi (10.34 MPa), the question arises if such unique surface features are indeed closely linked to the onset of the mesa burning rate trend at 2000 psi (13.8 MPa).

The present work is aimed at addressing this question. It involves examination of surface features obtained by both quench methods, on both single crystals and pressed pellets of AP, over the pressure range 400–2300 psi (2.76–15.85 MPa). The upper limit on the range of test conditions is due to perceived limitations of the apparatus used, particularly in carrying out the dp/dt tests. However, note that the range covers the onset pressure of mesa burning rate trend, that is, 2000 psi (13.8 MPa), and thus, it helps in establishing a direct link between the mesa burning rate trend and the peculiar deflagration behavior.

Experimental Details

Test Samples

Samples of both single crystals and pressed pellets of AP were used in the present study. The samples were nominally in the shape of rectangular laminas, about 1.5–2 mm thick and 3–5 mm wide on the burning surface, and about 10 mm long. The single crystal samples were void-free ultrapure laminas cleaved from larger samples supplied originally by Boggs, as described in Refs. 1, 4, and 10. The large crystals were stored in an airtight dessicator. The samples of pressed pellets were cut from 1.5–2 mm thick disks prepared by hard pressing Kerr McGee AP powder of ultra-high purity (99.7% pure). The as-received powder was ground in a vibrating sample mill for 8 min to decrease its particle size to a nominal value of 30 μm (wide-cut distribution) before hard pressing. Pressing was done in a steel die assembly containing approximately 1.6 g of the ground powder in a hydraulic press at 31,930 psi (220 MPa) for 2 h or longer. The pressure and the duration are higher/longer than what is prescribed by Boggs et al.[11]

Experimental Methods

Testing was mainly in the form of interrupting burning samples by one of the two methods of quenching, followed by examining the quenched surfaces in the SEM. Both dp/dt-quench and thermal-quench methods were adopted in the present study. In all cases, tests were run in a nitrogen-pressurized vessel. In the dp/dt-quench tests, the pressure vessel was equipped with a Mylar® burst diaphragm at the top (well above the burning surface). Sample ignition and Mylar disk burst were accomplished by heating of nichrome wires with a suitable delay time between the two events. The pressure decay rates in the dp/dt-quench tests were of the order of 10^5 psi/s ($\sim 10^3$–10^4 MPa/s), similar to that reported by Boggs et al.[4] In the thermal-quench tests, the test sample was mounted between two copper blocks in a vicelike arrangement, with the sample protruding several millimeters above the copper blocks (similar to Refs. 1, 4, and 6). Each of the copper blocks is 13 mm wide, 4.75 mm deep, and 3.5 mm thick. Quench occurred spontaneously when the deflagration front reached the copper heat sinks. All samples in all of the tests were initially at ambient room temperature, nominally 21°C.

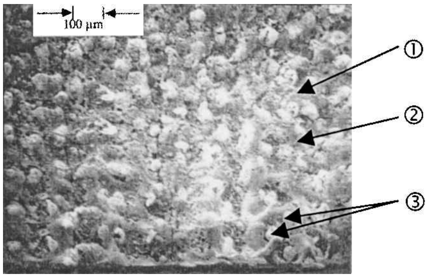
Results

Surface Features During Normal Deflagration

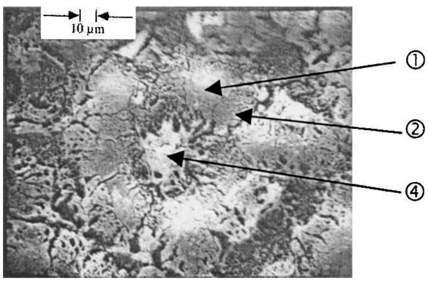
We begin by presenting results corresponding to normal burning behavior of both single-crystal and pressed AP over the 400–2000 psi (2.76–13.8 MPa) range. Figure 2 contains an array of SEM images that show the normal burning behavior at selected pressure levels. Particularly, Figs. 2c and 2d are obtained at the same pressure, namely, 2000 psi (13.8 MPa), but with a single-cyrstal sample and a pressed pellet sample, respectively. These highlight the equivalence in the surface features of the two types of samples, as reported by Boggs[1] and Boggs et al.[4] The images in Fig. 2 correspond to quenched surfaces of samples obtained by the dp/dt-quench method. The features seen here are exactly similar to those reported earlier,[1,4,6] obtained by this method up to 1200 psi (8.27 MPa). The features include the presence of large-scale ridges and valleys that macroscopically present the view of a fingerprint pattern. Additionally, froth and pores and burst bubbles are present at different parts of the surface, particularly at locations that are somewhat recessed. The prevalence of these additional features decreases even as the contrast in the overall fingerprint pattern becomes sharper, as the pressure is increased in the range considered. This has been confirmed by additional tests using the dp/dt-quench method at more intermediate pressure levels such as 1500 psi (10.34 MPa) and 1800 psi (12.40 MPa), results of which are not shown here. More of these images and associated explanation are reported in Ref. 12 in great detail. The most important aspect to note is that the overall surface is not macroscropically uneven, and there are no sites of needle formation in the entire pressure range 400–2000 psi (2.76–13.8 MPa).

Surface Features During Anomalous Deflagration

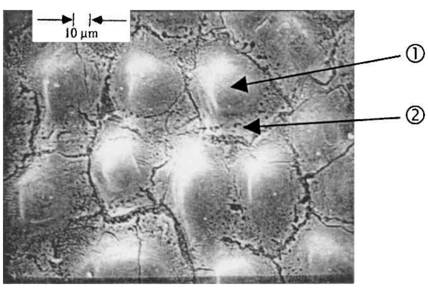
Test samples of single crystals and pressed pellets of AP were dp/dt-quenched at 2300 psi (15.85 MPa). This pressure level is clearly within the regime of the mesa burning rate trend in Fig. 1. SEM images of a test sample of pressed AP are shown in Fig. 3. Figure 3b is a magnified view of the right-top portion of Fig. 3a. It can be seen that the surface is very uneven on a macroscopic scale and contains arrays of needles in sporadic pockets. These are clear symptoms of anomalous deflagration behavior. This behavior is seen in both single crystals as well as pressed pellets of AP.



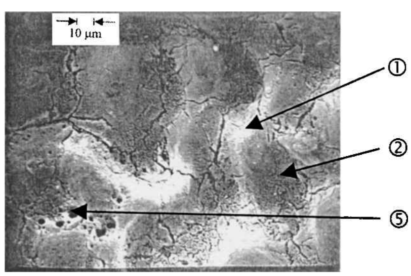
a) Single crystal at 400 psi (2.76 MPa)



b) Pressed pellet at 1000 psi (6.89 MPa)



c) Single crystal at 2000 psi (13.8 MPa)

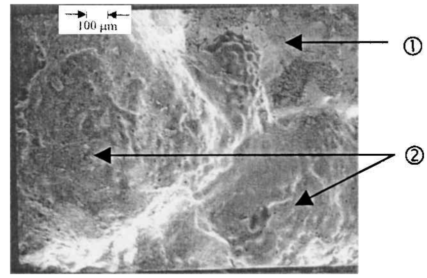


d) Pressed pellet at 2000 psi (13.8 MPa)

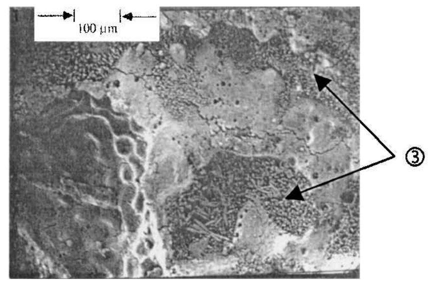
Fig. 2 Surface features of AP samples quenched by rapid depressurization: ①, ridges; ②, valleys; ③, bubbles; ④, froth; and ⑤, pores.

Surface Features of Thermally Quenched Samples

In contrast to the preceding results, the SEM images obtained of thermally quenched samples, both single crystals and pressed pellets of AP, show signs of anomalous deflagration at much lower pressures than the onset of mesa burning rate trend. Figure 4 shows these images. All of the images show the presence of needle arrays to different extents. Figure 4a shows a very different surface feature than what is observed in Fig. 2a obtained by dp/dt-quench at the same pressure, that is, 400 psi (2.76 MPa). Figure 4b shows a specific region on the surface of the sample thermally quenched at 400 psi (2.76 MPa) containing a small array of needles. The image in Fig. 4c, of sample tested at 1000 psi (6.89 MPa), also shows a large array of needles. These are unlike what has been reported in the past, and show the effect of the thermal-quench event rather dramatically. On the other hand, the presence of needles at 2000 psi (13.8 MPa) seen in Fig. 4d is similar to what has been reported earlier,[1,4,6] but



a) SEM image



b) Magnified top-left portion of image

Fig. 3 Surface features of pressed AP pellets quenched by rapid depressurization at 2300 psi (15.85 MPa): ①, retarded regression; ②, accelerated regression; and ③, array of needles.

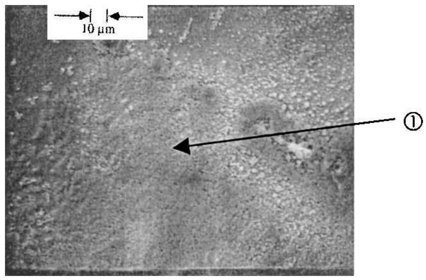
this is in sharp contrast with the normal-looking surface features in Fig. 2c, also of a single-crystal sample, and in Fig. 2d of a pressed AP sample (note the difference in magnification between the two sets of images). As a side note, results of this work reconfirm that both single crystals and pressed pellets exhibit the same behavior when subjected to thermal quenching, just as well as with dp/dt quenching.

Discussion

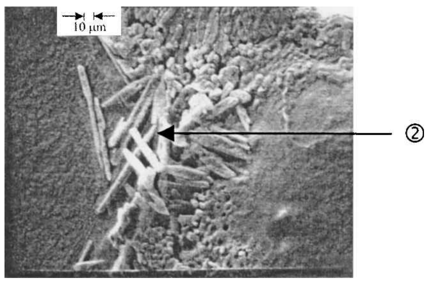
The results presented here show that the thermally quenched samples exhibit anomalous surface features at pressures well below the onset of the mesa burning rate trend of pure AP. The observation of such anomalous surface features at pressures below the onset of the mesa burning rate trend has been a source of confusion in establishing a link between such surface features and the burning rate trend. It is apparent that this has been because the thermal-quench method was adopted in past studies to obtain results in the crucial pressure range 1200–4800 psi (8.27–33.08 MPa). The present tests further reveal normal burning up to 2000 psi (13.8 MPa) and anomalous features above that pressure [at 2300 psi (15.85 MPa)], using the dp/dt-quench method. It is now possible to confirm a direct connection between the anomalies in the surface features and the burning rate trend.

It may appear reasonable to suspect that the dp/dt-quench event would cause disruption of the surface features during burning and may even eject the liquid layer off the burning surface. It may further be argued that such disruption may conceal any anomalous features such as needle formation that may be happening at low pressures as well. If this were so, formation of needles cannot be distinctly observed at 2300 psi (15.85 MPa), the highest pressure at which dp/dt-quench was adopted in the present study, where any disruption of the quenched surface is expected to be the most severe. On the other hand, the rapidity of the dp/dt-quench may be more effective in freezing the thin surface liquid layer. The prevalence of frozen remnants of burst bubbles on the quenched surfaces has been corroborated by high-speed cinematography of formation of froth and bubbles, at low pressures.[10] When these are considered, the dp/dt tests are not suspected to have any misleading artifacts.

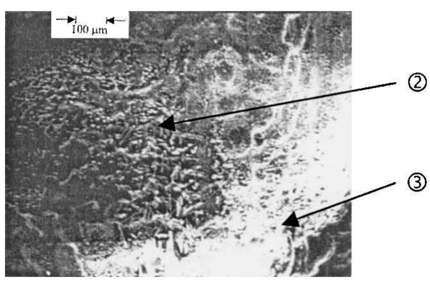
On the other hand, the needle formation is more evident in the thermally quenched samples than in dp/dt-quenched samples, particularly at low pressures. Although the processes undergone by the sample subjected to the thermal-quench processes are real, they are



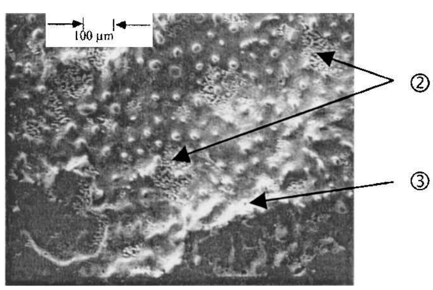
a) Single crystal at 400 psi (2.76 MPa)



b) Single crystal at 400 psi (2.76 MPa) different location on the surface



c) Pressed pellet at 1000 psi (6.89 MPa)



d) Single crystal at 2000 psi (13.8 MPa)

Fig. 4 Surface features of AP samples quenched by the thermal-quench method: ①, dry parched surface; ②, array of needles; and ③, macroscopically uneven surface regression.

not observed in high-speed cinematography of freely burning samples at low pressures. In view of this, the needle formation observed in thermally quenched samples at pressures lower than the onset of the mesa burning rate trend is considered to be an artifact of the slow quench transient experienced in the thermal-quench method. Such artifact induced in the thermal-quench process in the present work certainly appears more severe than that prevalent in the past works, probably because of smaller sample thickness relative to that of the copper blocks adopted in the present study compared to the past studies.

Note that this artifact of the slow thermal-quench process at low pressures, that is, sporadic sites of needle formation, is identical to that observed in the anomalous combustion regime of pure AP just above 2000 psi (13.8 MPa). This gives a clue to the conditions that are conducive to needle formation, that is, the need for lateral heat loss locally at sites surrounding the pockets of needles, resulting in local retardation of the surface regression and, thus, an uneven regression of the overall surface. The lateral heat loss is provided by the copper heat sinks in the thermal-quench tests, but is naturally prevalent in localized regions at pressures above the onset of mesa burning rate trend, resulting in decrease of the rate of regression of the overall surface. This is supported by the observation of Glaskova and Bobolev[5] that the onset of mesa burning rate trend is shifted to higher pressures with increase in the initial temperature of the sample. It is possible that the additional thermal energy available at higher initial temperatures mitigates the occurrence of large-scale heat loss lateral to the overall surface until higher pressures are reached. It must be remembered that none of these considerations, however, are sufficient to completely explain what triggers the anomalous behavior itself.

The role of lateral heat loss in triggering anomalous combustion behavior of AP is significant in the context of composite propellant combustion, where conventional hydrocarbon binders undergo endothermic decomposition and act as local heat sinks on the peripheries of AP particles adjoining their layers in the propellant burning surface.[13]

Conclusions

Fresh experiments performed on single crystals and pressed pellets of AP by rapid depressurization as well as thermal quenching methods in the 400–2300 psi (2.76–15.87 MPa) range have showed that nonuniform burning and formation of needles on the burning surface are more closely associated with the anomalous mesa in the deflagration rate of pure AP above 2000 psi (13.8 MPa) than reported in the past studies. Observations of these features at pressures lower than 2000 psi (13.8 MPa) reported in past studies appear to be an artifact of the thermal quenching method.

References

[1] Boggs, T. L., "Deflagration Rate, Surface Structure, and Subsurface Profile of Self-Deflagrating Single Crystals of Ammonium Perchlorate," *AIAA Journal*, Vol. 8, No. 5, 1970, pp. 867–873.

[2] Glaskova, A. P., "Anomalies in the Burning of Ammonium Perchlorate and Ammonium Nitrate," *Fizika Goreniya i Vzryva*, Vol. 4, No. 3, 1968, pp. 314–332.

[3] Varney, M., "An Experimental Investigation of the Burning Mechanism of Ammonium Perchlorate Composite Solid Propellants," Ph.D. Dissertation, School of Aerospace Engineering, Georgia Inst. of Technology, Atlanta, GA, May 1970.

[4] Boggs, T. L., Price, E. W., and Zurn, D. E., "The Deflagration of Pure and Isomorphously Doped Ammonium Perchlorate," *Proceedings of the Thirteenth International Symposium on Combustion*, Combustion Inst., Pittsburgh, PA, 1971, pp. 995–1008.

[5] Glaskova, A. P., and Bobolev, V. K., "Influence of the Initial Temperature on the Combustion of Ammonium Perchlorate," *Doklady Akademii Nauk SSSR*, Vol. 185, No. 2, 1969, pp. 346–348.

[6] Boggs, T. L., and Kraeutle, K. J., "Role of the Scanning Electron Microscope in the Study of Solid Rocket Propellant Combustion. I Ammonium Perchlorate Decomposition and Deflagration," *Combustion Science and Technology*, Vol. 1, 1969, pp. 75–93.

[7] Glaskova, A. P., "Effect of Pressure on the Combustion Rate of Ammonium Perchlorate," *Zh Prikl Mekhan i Tekhn Fiz*, Vol. 5, 1963, pp. 121–125.

[8] Beckstead, M. W., Derr, R. L., and Price, C. F., "A Model of Composite Solid-Propellant Combustion Based on Multiple Flames," *AIAA Journal*, Vol. 8, No. 12, 1970, pp. 2200–2207.

[9] Price, E. W., Chakravarthy, S. R., Sigman, R. K., and Freeman, J. M., "Pressure Dependence of Burning Rate of Ammonium Perchlorate–Hydrocarbon Binder Solid Propellants," AIAA Paper 97-3106, July 1997.

[10] Hightower, J. D., and Price, E. W., "Combustion of Ammonium Perchlorate," *Proceedings of the Eleventh International Symposium on Combustion*, Combustion Inst., Pittsburgh, PA, 1967, pp. 463–472.

[11] Boggs, T. L., Zurn, D. E., and Netzer, D. W., "Ammonium Perchlorate Combustion: Effects of Sample Preparation; Ingredient Type; and Pressure, Temperature, and Acceleration Environments," *Combustion Science and Technology*, Vol. 7, 1973, pp. 177–183.

[12] Price, E. W., Chakravarthy, S. R., Sigman, R. K., and Freeman, J. M., "Anomalous Combustion Behavior of Ammonium Perchlorate at Elevated Pressures," *Proceedings of the 33rd JANNAF Combustion Meeting*, Chemical Propulsion Information Agency, Laurel, MD, 1996, Publ. 653.

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