Ammonium Perchlorate and Ammonium Perchlorate—Binder Sandwich Combustion

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Theme

MANY analytical and experimental studies have been made of composite solid propellants which use ammonium perchlorate (AP) as the oxidizer. These studies have been made in an attempt to determine the controlling combustion mechanisms so that adequate modeling can be obtained. Two-dimensional propellant sandwiches have been used in order to provide a convenient means of studying a variety of propellant types under a wide range of test conditions, and they allow AP-binder interactions to be conveniently studied by visual methods.

In the past, most studies of AP-binder sandwich combustion and AP deflagration have been conducted by using high-speed motion picture photography and postfire examination of quenched samples.[2–8] In order to gain further needed knowledge of the behavior of AP *during* deflagration, Kennedy[1] conducted a schlieren investigation of AP-binder sandwich combustion. He found that a complex interaction occurred between the primary flame, AP deflagration, and binder pyrolysis products, and that the sandwich burner flames appeared to be laminar below the lower pressure deflagration limit (PDL) of AP and unsteady or "turbulent" above the PDL of AP. However, much of the results of that initial schlieren study were speculative because of the large schlieren optical depth and low film plane magnification that were employed.

In this investigation,[9] the experimental apparatus and the techniques used by Kennedy[1] were refined in order to improve the quality of the experimental data. The improved methods were used to study AP deflagration and AP-binder sandwich combustion. The behavior postulated from normal photography and quenched sample examination was examined with a technique which provided additional behavioral data during the actual combustion process.

Contents

Color schlieren studies were conducted in a nitrogen purged combustion bomb at pressures from 100 to 1000 psig. A high-speed (7500 PPS) color motion picture was taken for each test condition. Each film contained alternating frames of color schlieren and standard real-light color pictures. Propellant sandwiches were made from three grades of pressed polycrystalline AP and three different types of binder. Table 1 presents a summary of the tests conducted in this investigation. An edited color film has been prepared which includes segments of all AP and AP-binder sandwich films.

The color schlieren taken at 400 psig of pressed polycrystalline ultra-high purity (PP-UHP) AP, single crystal ultra-high purity (SC-UHP) AP, and pressed polycrystalline commercial grade (PP-COMM) AP all had blue and red schlieren color shifts just above the burner surface. These color shifts were on the order of 300 μ in width. The deflagration of all three burners appeared laminar, with a definite temperature peak above the center of the burner. The PP-COMM AP had a scalloped surface which accounted for a more unsteady appearance of the gas flow above the deflagrating AP. A yellow-green zone was visible within the SC-UHP AP extending from the burner surface to a depth of approximately 200 μ. This zone is thought to be related to the phase change from an orthorhombic crystalline structure to a cubic structure (the 243°C isotherm) as reported by Boggs and Kraeutle,[2] Hightower and Price,[3] and Beckstead and Hightower.[4] Beckstead and Hightower[4] found this phase change zone to be approximately 22 μ deep in single crystals of AP burned at pressures of 400 psi. The three studies just mentioned investigated quenched samples to determine the phase change zone thickness. The difference between their results and the results of this study may be due to removal of surface material during quench and/or to an inaccurate measurement of the penetration depth of the cubic structure obtained from the recrystallized quench samples. More likely, however, is the possibility of light scattering (due to small cracks, etc.) and/or other than phase change phenomena causing the larger thickness found in this investigation.

Color schlieren taken at 500 psig indicated that the gases above the deflagrating AP were more turbulent in appearance than at 400 psig. There was much more large scale mixing closer to the burner surface than at 400 psig. The characteristic alternating red and blue zones were again visible and were on the order of 300–400 μ in width. The subsurface zone appeared to be thinner than at 400 psig but was not well enough defined for accurate measurement.

Color schlieren taken at 800 psig showed that the deflagration was turbulent, with a more uniform temperature in the gases above the burner. The subsurface zone was very thin at 800 psig.

Color schlieren taken at 1000 psig of a SC-UHP AP burner showed that the deflagration was extremely turbulent as evidenced by an almost uniform color in the gases just above the burner surface. The subsurface zone was not visible at this pressure. Careful examination of the film revealed the presence

Table 1 Tests conducted

Propellant	Binder type	Binder thickness (μ)	Pressure (psig)
PP-UHP AP[a]	...	...	300–800
PP-COMM AP[b]	...	...	350–500
PP-COMM AP[c] w/TCP	...	...	400–1000
SC-UHP AP[d]	...	...	200–1000
PP-UHP AP	PBAA[e]	47–439	100–600
PP-UHP AP	HTPB[f]	37–94	300–500
PP-UHP AP	PU[g]	115	300–500
PP-COMM AP	HTPB	100	300–500
PP-COMM AP w/TCP	HTPB	90–94	300–500

[a] Pressed polycrystalline, ultra-high purity AP.
[b] Pressed polycrystalline, commercial grade AP.
[c] Pressed polycrystalline, commercial grade AP with TCP.
[d] Single crystal, ultra-high purity AP.
[e] Polybutadiene acrylic acid.
[f] Hydroxyl terminated polybutadiene.
[g] Polyurethane.

Received April 12, 1973; revision received Sept. 6, 1973. The film that serves to back this synoptic is available on loan from the authors upon direct request from them. This work was sponsored by Naval Ordnance Systems Command, ORD TASK 331-0071/551-1-332-303.

Index categories: Solid and Hybrid Rocket Engines; Combustion in Gases.

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of alternating red and blue shifts very close to the surface. These color shifts were estimated to be on the order of 150 μ in width but were very difficult to measure.

Comparison of the color schlieren taken of the single crystals indicated that the thickness of the subsurface zone associated with the crystal structure change (and/or other phenomena) decreased as pressure was increased in agreement with the results reported by Beckstead and Hightower.[4]

The discussion of laminar vs turbulent deflagration is somewhat debatable. At the intermediate pressures (500–800 psi), the gases were turbulent at some distance above the surface. However, close to the burner surface there may be a laminar region, i.e., there may be a "height to turbulence" as found in freejet flames. At 1000 psi, the deflagration appeared turbulent very close to the AP surface.

Two additional tests were made in order to further study the subsurface zone. A color schlieren was taken of SC-UHP AP burned at 500 psi in which the color matrix was horizontally positioned. The schlieren thus indicated density (temperature) gradients only in the direction normal to the burning surface. The same subsurface yellow-green colored zone was evident, indicating that the green color resulted from the back lighting through the altered crystal structure (the mercury light source has several strong lines in the yellow-green frequency range) and was not due to schlieren effects.

Another interesting observation was made from the aforementioned film. The AP appeared to be burning in a pulsating manner. The red schlieren color above the crystal (which indicated an increasing temperature) evolved uniformly like puffs of smoke from the entire surface.

One additional test was made to investigate the subsurface zone. A single pure crystal of AP was wrapped with a resistance wire and the wire heated to approximately 250°C with a bomb pressure of 200 psi (below the PDL of AP). At each point where the wire touched the crystal the yellow-green color was evident. These results indicated that the yellow-green subsurface region was associated with the orthorhombic to cubic phase change.

The blue to red alternating color shifts across the burner surface previously mentioned are thought to result from local zones of rapid density (or temperature) change, i.e., local reaction sites on the surface of the AP. Such local reaction sites have been reported by Boggs and Kraeutle[2] and Hightower and Price.[3]

Hightower and Price[3] reported surface depressions on the order of 150 μ in width on the burner surface of quenched samples burned in the range of 300–700 psi. The widths of the blue to red color shifts measured from schlieren photographs taken in this study were about 300 μ in width. These blue to red color shifts may either be local reaction sites that merge together or may be indicating the spaces between the reaction sites.

The distance between reaction site centers was relatively independent of pressure for pressures between 400 and 800 psig. However, there was a distinct change in the appearance of the gases above the deflagrating surface when the pressure was raised from 800 to 1000 psig. The distinct sites which were evident at 800 psig became quite small or nonexistent at 1000 psig. Boggs and Kraeutle[2] found from quenched AP that the surface structure changed between 800 and 1000 psi. Below 800 psi a continuous bubbling froth existed on the surface. At 1000 psi the froth was found only in the valleys of a closely spaced (~ 75 μ) ridge-valley surface structure. The fluctuating surface structure (melt, local reaction sites, etc.) is apparently the source for the observed gas phase turbulence. Thus, the schlieren observations of the gas phase during combustion appear to agree with the results obtained from quenched samples.

Impurities in the AP and whether single crystals or pressed polycrystalline wafers were used, did not appear to have a significant effect upon the distance between reaction site centers.

In the study of AP-binder sandwich combustion, the effects of binder type, binder thickness, AP purity, and pressure were considered.

Sandwiches made with PBAA and HTPB behaved in a very similar fashion with small amounts of binder flow. However, PU appeared to readily flow over the adjacent AP surface, causing the gases evolving from the surface to be more turbulent below the PDL of AP and the surface regression to be flatter above the PDL of AP.

Increasing binder thickness appeared to increase the height of the binder protrusion above the AP surface. The increased binder height caused larger visible flames and at pressures below the PDL of AP caused the gases evolving from the surface to be more laminar in appearance. The turbulence level in the AP decomposition products increased as pressure was increased from below to above the PDL of AP.

It was also observed that at pressures below the PDL of AP, the visible flame had a single closed structure with one peak temperature in the center above the binder. As the pressure was increased above approximately 350 psi the AP began to deflagrate. At a pressure somewhere between 400 and 500 psi (depending on binder type, etc.) the AP began to deflagrate more rapidly than the AP/binder flame, leaving a protruding binder. Once this occurred, the single closed flame was divided into a two flame structure, one on each side of the binder. These flames did not rise vertically above the surface, but rather were canted outward over the deflagrating AP as a result of the binder-protrusion. Thus, even without appreciable binder flow into the AP, the visible flames became unsteady or "turbulent" as a result of the AP deflagration products interacting with the AP/binder diffusion flame. Binder flow onto the AP appeared to further aggravate the situation, causing more visible "turbulence".

Sandwiches made with PP-COMM AP burned in a notched configuration. The notching effect resulted from the fact that the AP decomposition/deflagration rate for commercial grade AP was less than for UHP-AP. The impurities in commercial grade AP (notably sulfated ash and tricalcium phosphate) inhibit the deflagration rate. This notching lead to much surface generated turbulence for the sandwiches made with commercial grade AP.

These results indicate that the turbulence level of AP-binder sandwich combustion is a function of pressure, AP purity, surface configuration, and the degree of binder flow onto the AP.

In conclusion high speed color schlieren photography has been shown to be a valuable tool in the study of AP and AP-binder sandwich combustion. Behavior postulated from normal photography and quenched sample examination has been confirmed by examining the temperature profiles in the gas phase during actual combustion.

References

[1] Brown, W. E., Kennedy, J. R., and Netzer, D. W., "An Experimental Study of Ammonium Perchlorate-Binder Sandwich Combustion in Standard and High Acceleration Environments," *Combustion Science and Technology*, Vol. 6, 1972, pp. 211–222.

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

[3] Hightower, J. D. and Price, E. W., "Experimental Studies Relating to the Combustion Mechanism of Composite Propellants," *Astronautica Acta*, Vol. 14, 1968, pp. 11–21.

[4] Beckstead, M. W. and Hightower, J. D., "Surface Temperature of Deflagrating Ammonium Perchlorate Crystals," *AIAA Journal*, Vol. 5, No. 10, Oct. 1967, pp. 1785–1790.

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

[6] Boggs, T. L. and Zurn, D. E., "The Deflagration of Ammonium Perchlorate Polymeric Binder Sandwich Models," *Combustion Science and Technology*, Vol. 4, 1972, pp. 279–292.

[7] Varney, M. A. and Strahle, W. C., "Experimental Combustion Studies of Two-Dimensional Ammonium Perchlorate-Binder Sandwiches," *Combustion Science and Technology*, Vol. 4, 1972, pp. 197–208.

[8] Jones, H. E. and Strahle, W. C., "A Motion Picture Study of AP Sandwich Combustion," *8th JANAF Combustion Meeting*, CPIA 220, Vol. 1, 1971, pp. 95–100.

[9] Murphy, J. L. and Netzer, D. W., "Ammonium Perchlorate and Ammonium Perchlorate-Binder Sandwich Combustion," Rept. NPS-57 NT 73021A, Feb. 1973, Naval Postgraduate School, Monterey, Calif.