

Conclusions

Perhaps the most important conclusion is that considerably more, accurate physiological data will be required to render the numerical results more meaningful from a physiological standpoint.

The previous treatment presents an approximate, steady-state model of a human body cooled by parallel cooling tubes. The analysis illustrates that the shape of the flux distribution curve at the skin has negligible effect on the temperature distribution within the tissue. It also indicates that for high metabolic rates the required minimum temperatures may become too low for comfort if the cooling strips are too narrow. If the cooling tubes are spaced too widely apart, the assumption of no heat flux at skin surface between adjacent tubes may become invalid.

Further extension of this analysis should be the exploration of transient phenomena associated with the problem. Previous work by Chato and Hertig⁶ indicates that the thermal response time of the human body is relatively slow. Consequently, the steady-state solutions have only limited value if the thermal conditions, such as metabolic heat production, change frequently. This problem is under consideration by the authors.

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Spectra and Temperature of Propellant Flames during Depressurization

A. D. BAER* AND N. W. RYAN*

University of Utah, Salt Lake City, Utah

AND

E. B. SCHULZ†

E. I. du Pont de Nemours, Martinsville, Va.

A rapid-scanning spectrometer has been used to obtain emission spectra from composite propellant flames subjected to depressurization by use of rarefaction waves. A comparison of the transient-flame spectra in the 1.7 to 4.8 μ region to the spectra from steady-state flames indicates that, during the initial, rapid pressure drop, the ammonium perchlorate gasification rate was increased relative to the fuel-binder decomposition. Later in the transient, spectra characteristic of a more fuel-rich flame were observed. Transient flame temperature measurements were also made. The spectra and temperature data indicate that very severe disturbances of the combustion process can be tolerated without producing extinguishment. Data are presented which indicate that the disturbances due to changing pressure at low-pressure levels are more effective in producing extinguishment.

Introduction

A CONSIDERATION of the processes involved during extinguishment of a composite propellant by depressurization indicates that this phenomenon is one of unusual complexity. Attempts at experimental investigation or description by analytical methods are likely to meet with great difficulties. One must consider transient phenomena when the steady-state processes themselves are poorly understood; and one must cope with the essential nonlinearity of

the problem where extinguishment is achieved by large excursions in pressure. To be effective, these variations must occur in a few milliseconds. Propellant heterogeneity also enters the picture. Finally, it is even difficult to find an unambiguous experimental or theoretical criterion for completion of the processes (extinguishment). However, in spite of such difficulties, some experimental characterization of extinguishment has been possible and some success has been achieved in describing gross results by use of simple models.

Most experimenters¹⁻⁷ with ammonium perchlorate propellants have followed Ciepluch's¹ basic approach and have used small motors fitted with variable area or double nozzles. In such devices the depressurization rates are affected by the transient burning of the propellant. In other tests, burning strands were extinguished by imposing pressure decays, as by use of a rarefaction tube.⁸⁻¹¹ One of the defects of both approaches is that only partial information is obtained from each test. Either the flame is quenched or it persists; and

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* Professor of Chemical Engineering. Associate Fellow AIAA.

† Research Engineer.

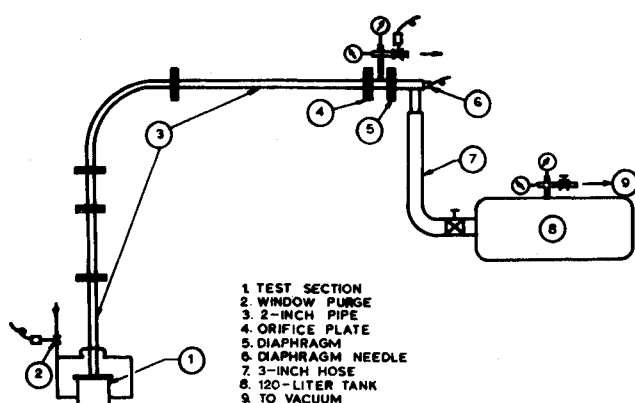


Fig. 1 A schematic sketch of the rarefaction tube system. The curved section is shown in place.

when it is quenched, spontaneous reignition sometimes occurs. Furthermore, in most cases it is not possible to determine the time or pressure at which burning ceased. Another uncertainty is the effect of the depressurization history since different conclusions are reached depending on whether the extinguishment criterion is taken as a critical value of the rate of pressure drop ($-dp/dt$), the time to half pressure, or the fractional rate of pressure drop ($-d \ln p/dt$). There is as yet no firm basis for selecting a preferred criterion.

Nevertheless, a fairly consistent qualitative picture emerges from extinguishment by rarefaction waves. For conventional propellant formulations, the slower burning propellants are extinguished by lower rates of pressure decay^{3,7,11} than are required for higher burning rate propellants. The fuel binder has a significant effect on the extinguishment requirement,^{3,4,6,7} and most investigations have indicated that the addition of burning rate catalysts increases the difficulty of extinguishment.^{3,9,10} The true effect of adding aluminum to a formulation is difficult to determine because the fuel-oxidant ratio is usually drastically altered, and the aluminum appears to act as a reignition source in most test devices.^{1,4}

For a single AP-fuel binder system, very simple solid-thermal-wave models appear to correlate well with experiment. The original von Elbe result,¹² when modified by inclusion of an adjustable parameter as suggested by Cohen,⁷ is remarkable in that only the normal burning rate law and this parameter are required to represent the results of the normal extinguish-nonextinguish test. The recent more complex models^{5,6,13,14} consider surface and gas-phase reactions, and for reasonable values of the reaction parameters agreement between experiment and theory is obtained.

In the present work, the measurements were intended to yield information concerning the extinguishment process, and they shed some light on such theoretical assumptions as homogeneity and quasi-static gas-phase processes. Also, it was anticipated that the interpretation of these measurements would suggest more subtle methods for producing extinguishment than by rapid and essentially total reduction of the pressure.

Emission spectra were obtained from combustion gases leaving propellant strands during rapid pressure transients. The emission intensity from the bands of the radiating gaseous species was taken as a measure of the species concentration. Flame temperature measurements were also made as an aid to interpretation of the spectral data.

Experimental Measurements

Spectrometer

Spectral measurements in this study were made by use of a Warner and Swasey Model 501 Millisecond-Scanning Spectrometer. A long- and short-wavelength region are simul-

taneously scanned and focused on a long- and a short-wavelength detector; the outputs from the spectrometer are in the form of time-varying electrical signals. It is possible to scan (in two parts) a continuous spectral region over a three to one wavelength range. Three dual spectral ranges (0.3–0.44 and 0.42–0.65, 0.65–1.15 and 1.10–1.75, and 1.75–3.2 and 3.1–4.8 μ) were used. In this study, both entrance and exit slits were set at 0.5 mm when data were taken in the 0.65- to 4.8- μ region, giving adequate spectral resolution and reasonable signal-to-noise ratio. When operated in the infrared ranges, the spectrometer was sealed and flushed with dry nitrogen to minimize atmospheric water and CO₂ absorption. In the visible range, 0.3–0.65 μ , 0.2 mm slits were used. The spatial region scanned was centered 1 cm in front of the 1.2–2.5-cm-diam strands. The angle of convergence to the optical beams was 8.5°. Thus the combustion gases under study were some distance from the propellant surface, and were presumably equilibrated.

Flame temperature measurements were made by setting the spectrometer to the sodium D-lines at 0.589 μ . A high-speed chopper was used to interrupt the focused light beam from a tungsten-filament lamp before it passed through the propellant-flame. In one second of operation, it was possible to produce 4500 interruptions of the beam from the lamp which was operated at an effective temperature of 2730°K. The light passed through the test section and was detected by the spectrometer. The spectrometer (now monochromator) output signal contained alternate emission, emission-absorption information which was converted into temperature results by reference to the pre-run intensity from the strip lamp.^{15,16}

Combustion Test System

The rarefaction tube used was made from flanged sections of 2-in. schedule-40 stainless-steel pipe. Straight tube lengths from 2–6 ft were employed. A 4-ft curved section was available which could be placed in the middle of the tube to give a maximum length of 16 ft. The test chamber, which was bolted to one end of the rarefaction tube, and the propellant sample holder which formed the closed end of the test section were machined from steel and chrome plated.

Figures 1 and 2 are sketches which illustrate the test section and the rarefaction tube system. The test section was fitted with two opposed sapphire windows for spectrometric observation and a port for a pressure transducer. The windows were kept clean by a flow of dry nitrogen. Two pressure transducers were used. The frequency response of both transducers was adequate to insure accurate pressure histories for this study, and the pressure signals from the two units were equivalent for similar conditions.

The outflow end of the rarefaction tube was terminated by an orifice plate. Pressure gages, a purge by-pass, and a solenoid for breaking the cellulose-acetate diaphragms, which

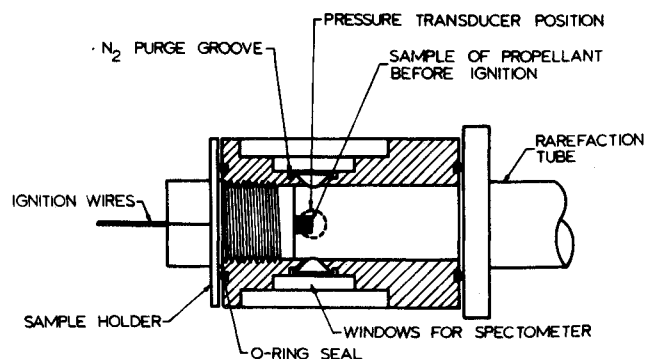


Fig. 2 A sectional view of the combustion test section. The inside diameter of this test section matches the 5.28 cm i.d. of the rarefaction tube shown on the right.

initially prevented flow through the orifice, were mounted at this end of the tube. Orifice diameters from 0.25 to 1.75 in. were used. After rupture of the diaphragm, gas flowed through the orifice into a dump tank which had a volume of 120 liters and was evacuated by use of a water aspirator.

Cylindrical samples of propellant about 1.2 cm in length and 1.75 cm in diameter were fitted into a 0.5-cm deep hole in the sample holder and secured in place by means of double-stick tape and a thin layer of cement. Carbon yarn was wrapped around the ignition terminals and passed through a small notch cut in the center of the propellant sample. Electrical heating of the yarn produced ignition without generating materials which would obscure the spectra or attack the windows. The sample burned for 1.0–3.0 sec, depending upon the type of propellant and the pressure, before the diaphragm was broken by a timer-controlled solenoid. At the time depressurization started, the sample surface was flush with the end wall of the rarefaction tube. High-speed motion pictures of the burning strands during rapid pressure drop showed a monotonic decrease in flame luminosity and confirmed the one-dimensional nature of the gas flow near the sample. No solid particles were ejected during the decay, and this observation was confirmed by the spectral measurements as the level of continuum radiation decreased relative to band radiation as the pressure dropped.

Data Acquisition

The spectrometer generated an enormous amount of data at the rate of 800 scans/sec. The detector preamplifiers have a band width of almost one megacycle, and the spectrometer resolution could be adjusted to produce information at the rate of nearly one million bits per second. Special techniques for recording and analyzing the spectrometer output were required. The recording problem was solved by the use of a Wollensak Model WF-22S Fastax camera as a strip camera to photograph an oscilloscope display.

The spectrometer and pressure-transducer outputs were displayed as vertically moving spots on a Tektronix Model 565 dual-beam oscilloscope, which was operated without time sweep. The camera was placed on its side and viewed the oscilloscope screen with the film moving normal to the vertical deflection of the oscilloscope trace. The peak film speed was about 20 fps; and, at this speed, the maximum length of a spectral display was 10–15 mm on the 16-mm film. The developed film presented the spectra with intensity across the film and wavelengths of the several scans along the length of the film. Reference 15 presents several examples of these spectral records. Pressure was also displayed as a third signal on the oscilloscope face by use of a dual channel plug-in unit, and the pressure signal appeared as a line of varying position on the developed film.

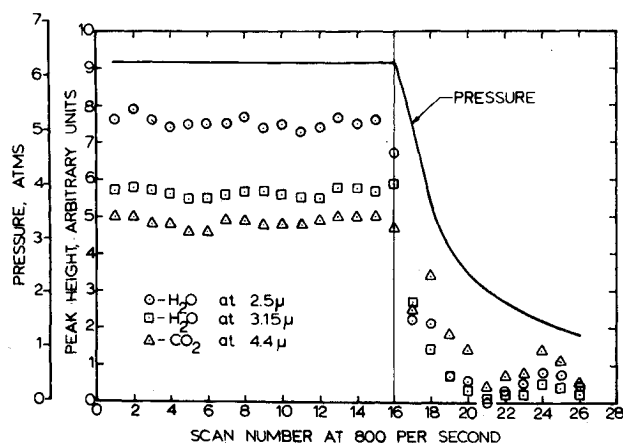


Fig. 3 Spectral data during steady-state burning and depressurization of the 82% AP-PBAA UCH propellant. No measureable radiation was detected after scan 26.

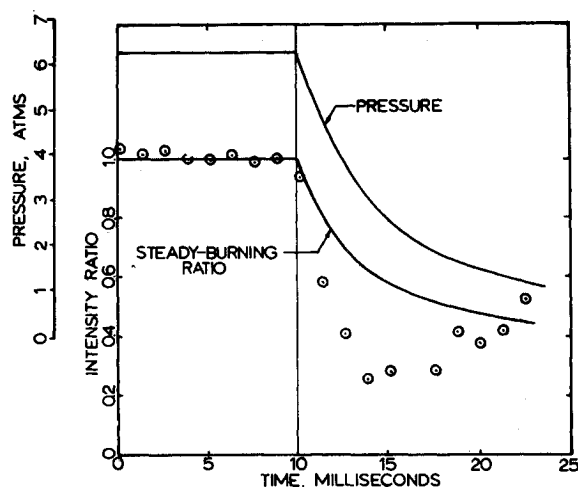


Fig. 4 Emission-intensity ratio of water at 2.5μ to carbon dioxide at 4.4μ during a depressurization test of the UCH propellant. Apparent flame extinguishment occurred after the last point plotted.

Propellants Studied

Details concerning the preparation and properties of propellants used in this study are presented in Ref. 15. Forty-six propellants were formulated, mixed, and cured for these tests. Polyurethane (PU), B. F. Goodrich Estane based, and the polybutadiene/acrylic-acid copolymer crosslinked with Epon (PBAA) binders were used. Commercial ammonium perchlorate (AP) manufactured by American Potash Co. was used in the propellants. Only three formulations, which exhibited characteristics typical of all materials considered, are discussed in detail here. These are the AP-PBAA propellants UCH (82% AP of equal parts -10μ and 200μ diameter and 18% fuel binder) and UAB (85% AP of 30/55 ratio of -10μ to 200μ) and the AP-PU propellant UCZ (80% AP of equal parts -10μ and 200μ). None of these formulations contained burning rate catalysts, although catalyzed systems were studied.

Experimental Results

Infrared Spectral Data

The most useful and unambiguous infrared emission bands were from water at 2.5μ , HCl at 3.7μ and CO_2 at 4.4μ . Emission from CO at about 2.4 and 4.8μ was too low in intensity to be consistently observed above the noise. A comparison of propellant-flame radiation showed that the AP loading had a pronounced effect on the general character of the infrared spectra. At low loading, 78% or 80% for the PBAA system, the continuous radiation, as indicated by the magnitude of the emission at wavelengths of minimum intensity in the scans, was high. This continuum is presumably from fine carbon particles, although equilibrium calculations indicate that solid carbon should not be present. At higher AP loading, 85%–86.5% AP, the continuous radiation was very low. Figure 3 illustrates the nature of the data obtained from a depressurization test in terms of the pressure and the measured emission peak heights at 2.5 (water), 3.15 (principally water) and 4.4 (carbon dioxide) μ . An apparent peak was obtained at 3.15μ which occurred at the "start" of the 3.1 – 4.8 spectral range. This emission was part of the broad water band which starts at 2.7μ . This 3.15μ peak was assumed to be water emission and was often used for reference purposes since the detector and amplifier through which the signal passed were the same as for the 4.4μ CO_2 band. Because the time of measurement of the 3.15μ emission and 4.4μ emission differed by almost 1 msec, comparison of these peak heights was difficult during a fast transient. The measure-

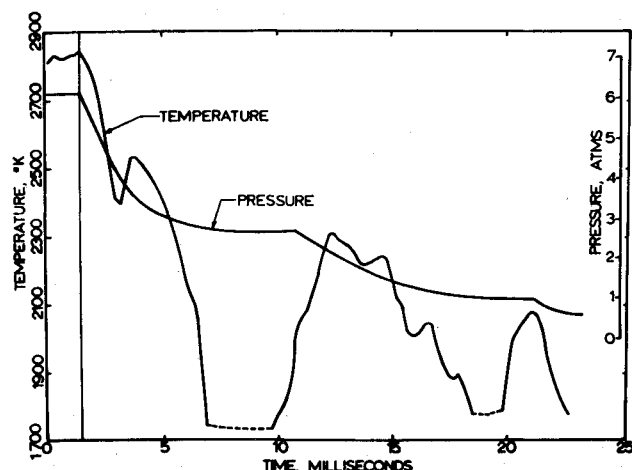


Fig. 5 Measured flame temperatures during a depressurization test of the 84.5% AP-PBAA UBC propellant which contained 1.5 NaCl in the fuel-binder. Extinguishment occurred after the third pressure drop.

ments of the 4.4μ and 2.5μ bands were almost coincident (within 0.2 msec) and direct comparison of these emissions was possible.

Two significant features are illustrated in Fig. 3. First, before start of the pressure decay, the magnitude of the intensity of the bands fluctuates, apparently as the result of almost periodic combustion irregularities. The major effect of these fluctuations was to limit the run-to-run comparison of data since the time at which depressurization started was not controlled relative to the fluctuations. Second, typically the intensities decreased rapidly as the pressure dropped and were often observed to increase prior to finally dropping to zero as in Fig. 3.

Because of the rapid pressure decay rates required to effect extinguishment, which also likely produced large flame temperature excursions, it was essentially impossible to translate emission data of the type presented in Fig. 3 directly into gas-phase concentration information. Interpretation of the emission data required another approach which was suggested by qualitative comparison of spectra during depressurization to the steady-state spectra from propellants containing differing levels of AP. It was early noted that as the pressure dropped the magnitude of the radiation from the continuous

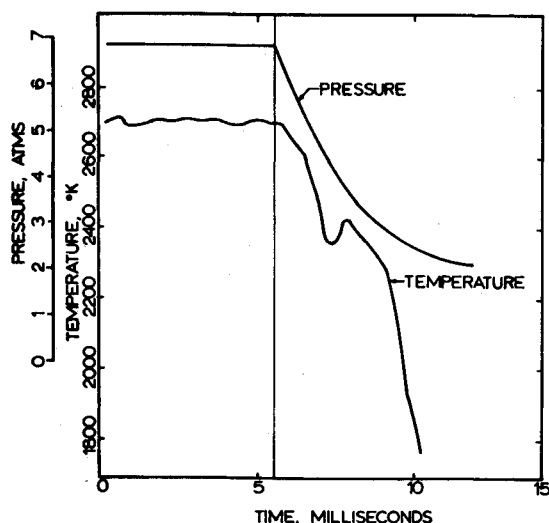


Fig. 6 Measured flame temperatures during depressurization of the 80% AP-PU, UCZ propellant (0.2% NaCl was added to the fuel binder). Extinguishment occurred during the first pressure drop.

sources (at about 2.3 and 4.2μ) significantly decreased relative to the emission from the carbon dioxide and water bands. Also, the height of the water peak relative to that of the carbon dioxide peak decreased. Both of these changes were characteristic of spectra obtained by increasing the AP content of a formulation. Equilibrium calculations also showed that the ratio of water to carbon dioxide in the propellant flame for these fuel-rich systems decreased as the AP level increased. It thus appeared that the effective AP loading to produce a propellant flame could be characterized by the magnitude of the continuous radiation and by the ratio of water to carbon dioxide emission. The use of the intensity ratios is related to the technique employed by Ferriso and Ludwig¹⁷ for measuring the water-to-carbon dioxide ratio in flames.

Figure 4 is a replot of the data from Fig. 3 in terms of the intensity ratios. These data are compared to this emission ratio determined from observation of steady combustion flames during slow pressure decay. In order to eliminate the effects of long time drift of detector sensitivity and electronic gains, the water-to-carbon dioxide ratios have been normalized to unity at the predecay value for these comparisons. The interpretation of the emission data in terms of the normalized intensity ratios by comparison to steady state is reasonably direct. By comparison of the transient to the steady state at the same pressure, the effect of self-absorption of the gas is treated since presumably the same pressure effect would be present. Also, by use of intensity ratios, the effect of temperature on emission is approximately treated since the temperature effect in the emission from the two bands would be similar. For the temperature and wavelengths of interest here, Planck's law indicates not much more than a direct dependence of intensity on absolute temperature, and this effect is partially offset by the effect of temperature on the concentration of gases.

The intensity ratios of the transient test, illustrated by Fig. 4, indicate that a more oxidizer-rich gas is produced during pressure decay. A few milliseconds later, as the rate of pressure drop decreases, a more fuel-rich gas is generated, in part as the result of depletion of oxidizer shortly before. In this test, and in many others, the termination of emission of radiation and presumed extinguishment occurred as the intensity ratio rose above the steady-burning values. This result suggests a rich mixture limit effect on flame extinguishment under some circumstances.

Temperature Measurements

A rational evaluation of transient emission data requires some knowledge of the transient radiating gas temperature.

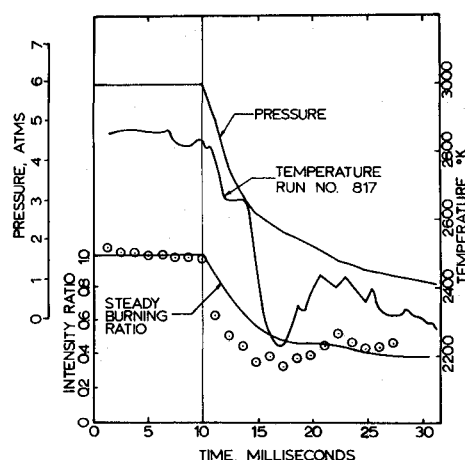


Fig. 7 Flame temperature and spectral intensity ratio (water at 2.5μ to carbon dioxide at 4.4μ) from two similar tests on the UAB propellant. In each case, extinguishment occurred at a later time than shown in this plot.

Consequently, flame temperatures were measured by use of the emission-adsorption technique at the sodium D-lines^{15,16} under extinguishment conditions. Ideally, the temperature measurements should have been made simultaneously with the spectral measurements. However, this approach would have yielded only half as many emission spectra; and during fast transients, even the 800 spectra per second rate was not high enough to define a continuous curve (see Fig. 4). Also, the maximum temperature of the available reference source (a silicon carbide element) was only about 1200°K, unuseable as a reference for the 2200°–2800°K flames. By use of the special high-speed beam chopper and the tungsten strip lamp on the source unit, operation of the spectrometer as a monochromator, and use of sodium seeded propellants it was possible to make accurate temperature determinations at the rate of 4500/sec.

Figure 5 illustrates the observed variation of the measured flame temperature (as a continuous curve) during depressurization. The average steady-state combustion temperatures measured prior to depressurization were in excellent agreement with calculated adiabatic flame temperatures. In the case illustrated by Fig. 5, the average measured temperature was 2825°K and the calculated value was 2810°K. The reference temperature in all cases was the effective filament temperature of the tungsten strip lamp, which was set at 2730°K. In the test section, the effective temperature of the filament image was 50–100°K lower than this value; the use of the uncorrected filament temperature as a reference apparently compensated for the factors which tend to reduce the measured temperatures such as temperature gradients, etc. Since the variations in flame temperature were of prime interest, no additional adjustments or corrections were made to the data.

Typically, the measured temperatures remained constant after start of pressure decay for 0.5–1.0 msec for low-AP propellants and 0.1–0.2 msec for high-AP formulations. The rapid temperature drop and short period of recovery 1–2 msec after start of the temperature decline shown in Fig. 5 is typical of all observations. The subsequent decrease in temperature to a value too low to be measured and the subsequent recovery and increase in temperature during the pressure plateau was also normally observed. An interesting pressure-temperature relationship is illustrated in Fig. 5 at the time of the second pressure drop. Although the pressure starts to decrease, the rate of temperature rise actually increases. Spectra data from similar tests indicate that the flame should be fuel-rich at the time the second pressure drop begins. It is speculated that the first effect of the second pressure decay is to increase the AP decomposition rate, thus increasing the oxidizer concentration in the gas phase. The resultant more nearly balanced fuel-oxidant stoichiometry leads to an increase in flame temperature. Although the rate of pressure decay induced by the last step in Fig. 5 was quite small, it was sufficient to produce final termination of the flame. It was often observed that such small pressure drops at low pressures appeared to be immediately followed by flame extinguishment.

Although it can be assumed that the measured steady-state temperatures were significant and accurate because they can be checked against calculated values, there is no direct method for checking the measured temperatures during the pressure transient. However, the only significant difference between the steady-state and transient measurement is the possible difference in transit time for combustion products between the propellant surface and the common plane of focus of the spectrometer and the radiation source unit; and, it can be shown that accurate steady-state values were obtained under more adverse conditions than were most of the transient values. First, the measured steady-state values did not change as the sample surface regressed from 0.5 to 1.5 cm from the focal position of the spectrometer beam. This result is consistent with measurements in Ref. 16, p. 103. All transient

measurements were made with 1.0 cm separation. Second, measured steady-state temperatures agreed with the calculated values at pressures of at least 0.2 of the initial pressures used in most of these tests (6.5–6.8 atm). Because of the pressure effect on the burning rate and the gas velocities, the transit time was reduced by less than a factor of two to three at low pressures (for pressure exponents of 0.3–0.5). Also because of the reduced density, the rate of the gaseous reactions would be greatly diminished at the low pressures. Nevertheless the 1 cm separation was adequate to insure near-equilibrium of gas-phase reactions. During the transient, the effect of the pressure decay on the mean stream velocity between the sample surface and the focal plane was determined. The approximate "centered-wave" theory as presented by Mitchell¹⁸ was used. For the range of variables of interest, the approximate theory is adequate. The exact theory (Rudinger¹⁹), which is harder to apply, is not needed. These calculations show that at high pressure during the rapid pressure decay, the mean velocity between the surface and focal plane is increased by a maximum factor of two, and the transit time was at worst equal to that of the low-pressure steady-state values. At low pressures during a transient test, pressure decay rates were low, and the increase in velocity as a result of the rarefaction is negligible.

If the initial pressure decay rate is high enough, recovery of the flame temperature during the pressure plateau does not occur. This effect is noted in Fig. 6 which summarizes the results of a test on the slower burning AP-PU propellant. Again, the curious partial recovery 1 to 2 msec after the initial temperature drop is noted.

Spectral and Temperature Measurements

Because the transient flame temperatures varied so drastically during depressurization, it is necessary to consider this effect on the emission spectra. Although simultaneous spectra and temperature measurements were not made, the run-to-run reproducibility of the test was good enough to permit a comparison of spectral and temperature measurements under the same test conditions. Figure 7 shows data from such runs. The pressure histories of the spectra and temperature test were essentially the same. These comparisons show that the drop in the spectral intensity ratios precedes the major drop in temperature, and that later the rise in the intensity ratio occurs at about the same time as the temperature recovery.

The large temperature changes have two expected effects on the spectral intensity ratios which must be accounted for. Because intensities from two wavelengths (2.5 and 4.4 μ) determine the intensity ratio, it is necessary to consider the effect of this difference in wavelength. In the hypothetical case in which the steady-state flame temperature is decreased at constant composition, Planck's law predicts that the intensity at 2.5 μ would decrease relative to the intensity at 4.4 μ . The maximum change in the intensity ratio would be only 10–15%, and the steady burning ratio line in Fig. 7 is corrected for this effect. The measured decrease in intensity ratio is still initially greater than for the steady-state case at the same temperature and pressure. The other effect is the equilibrium composition change. The equilibrium water-to-carbon dioxide ratio in these flames is determined by the AP-to-binder ratio and also the gas temperature. For constant gas phase atomic composition, the water-gas-reaction equilibrium determines the relative amounts of water and carbon dioxide for the propellant gases; and thus while there is then no effect of pressure change, the small change of the equilibrium constant with temperature yields a decrease in the water-to-carbon dioxide concentration ratio, and presumably a decrease in the intensity ratio, as the temperature drops. The relationship between the changes in intensity ratio produced by variation in the concentration ratio can only be estimated. However, this effect is small and detect-

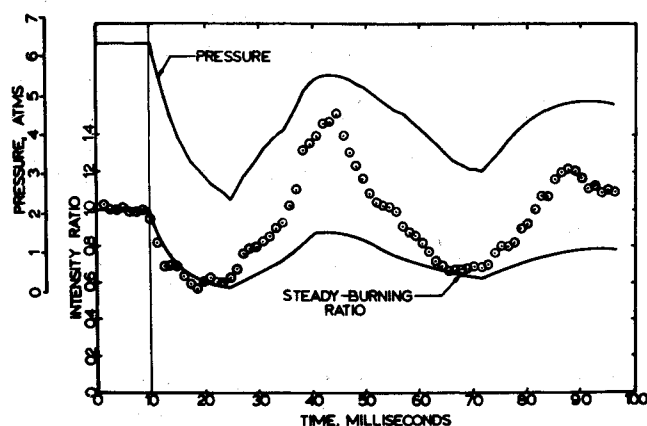


Fig. 8 Spectral intensity ratio of water at 2.5μ to carbon dioxide at 4.4μ of the 86.5% AP-PBAA UCX propellant during periods of fluctuating pressure.

able only after a temperature drop of 300–500°K, and is most significant for formulations containing lower AP levels.

Further Studies

The interpretation of the decrease of the water-to-carbon dioxide intensity ratio during rapid pressure decay as evidence for the effective decrease of the fuel-to-oxidant ratio in the gas phase during pressure drop appears to be justified. The evidence for the later occurrence of a compensating more fuel-rich gas is even stronger. In all cases after the initial pressure drop, the intensity ratio rose above the steady-burning value although the flame temperature remained below the steady-state values. Any temperature corrections would further increase the observed rise in the ratio. Also, the increase in intensity ratio always occurred at about the time that the surface AP crystals would be depleted by higher than normal regression rates. This effect is particularly apparent in the data shown in Fig. 8. Here a high AP propellant (86.5% AP in PBAA) was subjected to both falling and rising

Table 1 Effect of final system pressure on depressurization extinguishment of UCH propellant^a

Tube length 5 ft, nozzle area ratio 0.083		
Initial pressure, atm	Final pressure, atm	Extinguished
5.45	0.415	yes
5.45	0.422	yes
5.45	0.422	yes
5.45	0.422	yes
5.45	0.425	no
5.45	0.441	yes
5.45	0.445	no
5.45	0.448	no
5.45	0.448	no
2.02	0.428	yes
2.02	0.428	yes
2.02	0.461	no
2.02	0.545	no

^a For this propellant the low-pressure deflagration limit is 0.047 atm.

pressure by discharging the rarefaction tube into a small tank. Such a highly loaded propellant produces combustion gases nearly stoichiometric to water and carbon dioxide. Little decrease in the intensity ratio occurred during the pressure drop as a result of increased oxidizer content of the gas; however, after depletion of the surface ammonium perchlorate, the character of the flame is totally altered by the necessity to consume the excess surface fuel-binder during a period of rising pressure. In this case the intensity ratio actually rises above the initial value although the pressure and temperature (as measured in other tests) are substantially below their initial values. No explanation of such behavior, other than a large compositional change, appears reasonable.

Somewhat more direct evidence for compositional changes in the combustion gases during depressurization was obtained by operation of the spectrometer in the visible region to detect metallic ions which were compounded separately in the AP and fuel-binders to "tag" these components.

Figure 9 presents data from a test on the UAF propellant which was formulated with 16.8% of the PBAA polymer, 0.85% of fine NaCl dispersed in the polymer, and 81.3% of cocrystallized AP-KMnO₄ (97% AP). As the pressure initially dropped, the emission from the sodium dropped relative to the emission from the oxidizer-derived manganese. During the pressure plateau, the sodium emission relative to the manganese rose above its initial predepressurization value. These results confirm the interpretation of the infrared data.

Discussion and Conclusions

Significant variations in the gas-phase composition from a burning composite propellant are produced by rapid depressurization. Initially, higher than steady-state oxidizer levels are observed, and later a more fuel rich period occurs. Wide variation in the flame temperature is also noted. Although the temperature fluctuations are influenced by the compositional changes, order of magnitude arguments¹⁵ show that the major cause of the temperature drop is the necessity of increasing the feedback flux to the solid to accumulate energy as the burning rate drops while at the same time the rate of thermal energy generation is also decreasing as a result of the lower regression rates. For the fuel-rich propellant systems considered, the initial effect of the compositional changes would be to increase the oxidizer species and to increase the flame temperature. However, this effect is apparently overwhelmed by the energy accumulation requirement although the partial recovery in the temperature which was noted 1–2 msec after the initial temperature drop may be the manifestation of these two opposed and simultaneous processes.

The assumptions of a time-invariant gas-phase composition and a homogeneous solid which are usually made to yield

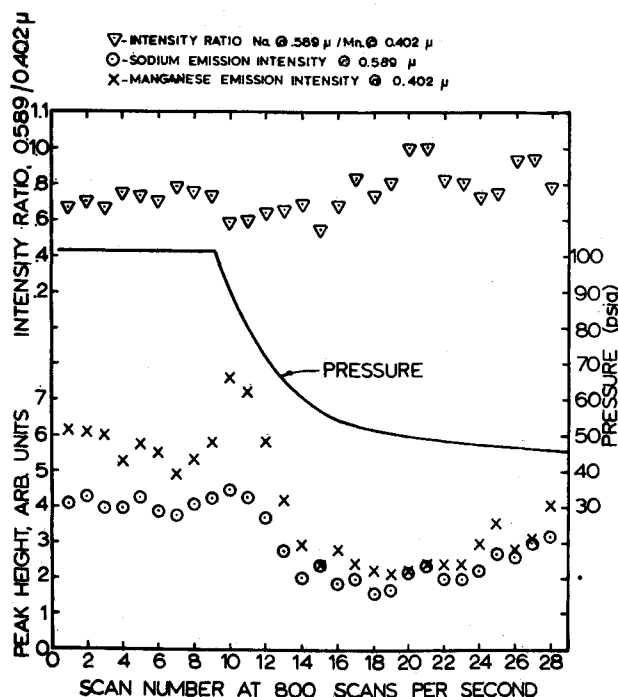


Fig. 9 Emission from sodium and manganese from the flame of special AP-PBAA UAF propellant during depressurization.

tractable theoretical models appear to be particularly poor when applied to composite propellant extinguishment. Unless the gas-to-solid energy feedback mechanism is totally independent of the gas-phase composition and the relative rates of gasification of the propellant constituents, theoretical models based upon these assumptions cannot be accurate in detail.

The ability of the solid propellant combustion process to tolerate rapid pressure changes which produced significant compositional and enormous flame-temperature variations and to then recover and adjust to steady-burning at a lower pressure is quite remarkable. In these tests no source of reignition was present. Normally, when extinguishment did occur, the relatively slow pressure changes which occurred at low pressures were directly responsible. In all cases, extinguishment pressures were at least an order of magnitude greater than the low-pressure deflagration limits.

The importance of the processes at low pressures is shown in the data presented in Table 1 in which only the dump-tank pressure was varied from run to run. Extinguishment or nonextinguishment was observed depending on the final tank pressure although the initial pressure-decay rates were the same; and in fact, the total pressure history [expressed as $p/p_0 = f(t)$, where p_0 is the initial pressure] was identical for all tests until the orifice flow became subsonic. If it is true that most extinguishments are more strongly affected by the pressure changes at low pressures than by initial faster depressurization, the apparent agreement between simple theory and experiment can be explained. By the time that the low pressures are reached, the processes are slow enough that the assumptions of one-dimensionality and homogeneity become more acceptable. The experimental factors which determine the initial rates also determine the total transient and the slow processes. Thus, it would be possible to correlate in terms of the initial or average rates even though the low-pressure processes are controlling. This apparently is what has occurred. But, although the theoretical models represent sound dimensional analysis and are useful for correlation purposes, they do not describe the phenomena, and therefore may have limited predictive value.

Although the experimental data presented here suggests an intractable theoretical model, these results do improve the understanding of the process and do suggest approaches for improvement in extinguishable propellants and in depressurization extinguishment systems. In order to take advantage of the disproportionation during rapid pressure change, the fuel-binder should be selected to have minimum interaction with the ammonium perchlorate during combustion to take advantage of likely different pressure dependencies of the decomposition of the ingredients. For the same reason, simpler formulations should be more easily extinguished by rapid pressure drop since coupling between the AP and polymer gasification is more likely in the presence of additives.

These data suggested that very severe conditions are required to produce extinguishment in the first few milliseconds of the decay. The momentarily-increased rate of AP gasification tends to improve the flame stability of the fuel-rich systems. On the other hand, high-oxygen-content binders with high AP loadings might exhibit an opposite effect. The fuel-rich systems should be most susceptible to extinguishment after depletion of the surface AP crystals, and two step depressurization might be practical in which the first drop

disrupts the gas-phase composition and a delayed second drop extinguishes the unstable flame.

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