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Spectral Studies of
Solid Propellant Combustion
IV: Absorption and Burn Rate Results
for M43, XM39, and M10 Propellants

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13. ABSTRACT (Maximum 200 words) An optical absorption experiment coupled to a windowed strand burner has been used to obtain dark zone temperatures and nitric oxide concentrations for two nitramine propellants (M43 and XM39) and a single base propellant (M10). Moreover, burn rates as a function of pressure were determined from the video record of the propellant burns. These measurements were taken over a pressure range from 0.8 to 2 MPa.				
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1. INTRODUCTION

Over the past five years we have been gathering combustion diagnostic information from the burning of solid propellants over a pressure range of 0.1 to 2.0 MPa (Vanderhoff 1988, 1989, 1991; Vanderhoff, Kotlar, and Teague 1990; Vanderhoff, Teague, and Kotlar 1991, 1992; Vanderhoff and Kotlar 1990a, 1990b; Teague and Vanderhoff 1991; Vanderhoff, Anderson, and Kotlar 1992). The experimental technique has been optical absorption. The region of recent focus has been the dark zone since the spatial resolution requirements are relaxed and more within the present capabilities of the experimental arrangement. This information is used in testing or validating combustion models of the dark zone that include detailed chemistry (Sotter 1965; Fifer et al. 1990; Vanderhoff, Anderson, and Kotlar 1992). We report here burn rate and absorption results for two low vulnerability nitramine propellants and a single-base propellant. See Table 1 for a description of the ingredients.

2. EXPERIMENTAL

The experimental apparatus and technique is the same that has been described recently (Vanderhoff, Teague, and Kotlar 1992), except for the change in the method of ignition which will be described here. A cross-sectional view of the windowed strand burner is shown on Figure 1. The technique used to ignite the solid propellant samples has been changed from hot wire ignition to laser ignition. A nominal 25-W CO₂ laser coupled into the chamber with a ZnSe window readily ignites the propellant samples by using irradiation times of about 0.5 s. The propellant samples are solid cylinders with typical dimensions of 6.0 mm diameter and 20 mm length. The diameter of the laser beam is 3 mm, and is positioned with an adjustable turning mirror to impact the propellant center. This laser ignition feature simplifies the experimental procedure since installation of a wire ignitor is no longer necessary. The propellant sample must be moved into the absorption beam after a background spectrum is taken and frequent dislodging of the ignitor wire was a problem. After the propellant sample is ignited with the CO₂ laser, the absence of ignitor wire remnants removes possible perturbations such as flame holding.

The NO absorption data is composed of two vibrational hot bands that are not rotationally resolved. Thus, to independently deduce the detector response function or effective bandwidth (full width at half maximum - FWHM), an additional experiment was conducted using the 253.65-nm line of an Hg lamp as a narrow line light source. For a 0.32-m spectrometer with a 1,200 groove/mm grating operating second order, the bandwidth as a function of the spectrometer entrance slit setting is shown on Figure 2.

Table 1. Propellant Composition

Propellant	Ingredient	Weight (%)
M10	Nitrocellulose (13.16% N)	98
	Potassium Sulphate	1.0
	Diphenylamine	1.0
XM39	RDX ^a	76
	Cellulose Acetate Butyrate	12
	Acetyl Triethyl Citrate	7.6
	Nitrocellulose (12.6% N)	4.0
	Ethyl Centralite	0.4
M43	RDX ^a	76
	Cellulose Acetate Butyrate	12
	Nitrocellulose	4.0
	Proprietary Plasticizer	8.0

^a RDX - cyclotrimethylene trinitramine.

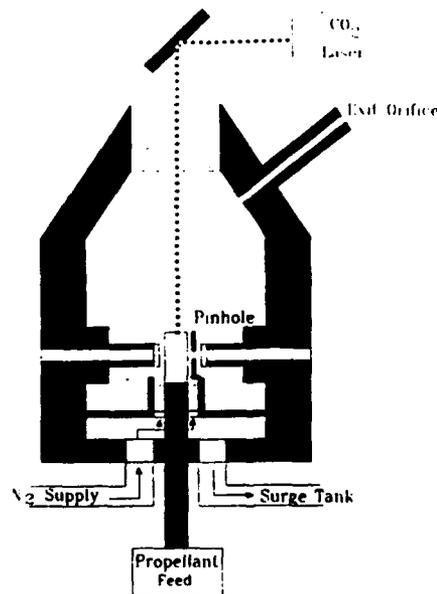


Figure 1. Cross section of chamber used to burn solid propellants at an elevated pressure of nitrogen. The laser ignition arrangement is also shown.

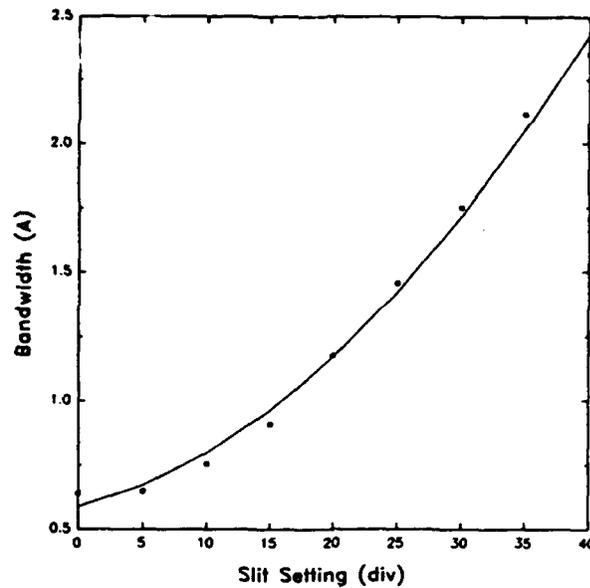


Figure 2. Measured bandwidth as a function of slit setting for a 0.32-m spectrometer operating second order with a 1,200 groove/mm grating.

The bandwidth is given in angstroms and the slit settings are represented by divisions where a division corresponds to 5 μm . Slit settings ranging from 15 to 30 were used for the NO absorption measurements; thus, the spectral resolution varied from about 0.8 to 1.7 angstroms. The spatial resolution was governed by the pinhole and is 200 μm .

3. RESULTS

Examination of video records of each propellant burn provided the necessary data for burn rate determinations of the three propellants studied: M10, XM39 and M43. These burn rates as a function of pressure are shown on Figures 3–5, where the solid line is a fit to the data using the standard burn rate equation, $r = aP^n$. Results for a and n and their standard deviations are given in the figure captions. At these low pressures, the single base propellant, M10, has a noticeably higher burn rate than either of the nitramine propellants. It is this low pressure-low burn rate characteristic that makes these nitramine propellants low vulnerability candidates. The higher burn rate of M43 is brought about by the use of an energetic plasticizer.

The only other low pressure burn rate data we are aware of for these propellant formulations is some unpublished work of Miller (1985). His experimental apparatus and detection technique is similar to the experiment reported here, however, the burn rates were measured over a larger pressure range—1 to 8 MPa nitrogen. Reasonable agreement is obtained for the nitramine propellants. For XM39, Miller obtains values of $n = 0.89$ and $a = 0.50$ and, for M43, the values are $n = 1.07$ and $a = 0.78$. A sizeable difference occurs in M10 for which Miller gives values of $n = 0.64$ and $a = 3.54$. These differences are not thought to be uncertainties in the experimental technique out rather differences that come from the propellant manufacturing process.

Determination of propellant dark zone temperatures and NO concentrations come from the absorption spectra of the NO molecule (Mitchell and Zemansky 1971). There is such an abundance of NO in the dark zone that (0,0) $A^2\Sigma - X^2\Pi$ transitions result in 100% absorption of the incident light. Thus, two hot vibrational bands [(0,1) and (0,2)] are used for the absorption measurements. A sample spectrum is shown in Figure 6. There are 531 data points and the solid line represents a least-squares fit to the data where 2,125 rotational transitions are considered in the fitting procedure. Various parameters including the temperature and NO mole fraction are allowed to vary to fit the data. A temperature of 1,419 K and an NO mole fraction of 0.11 provided the best fit to this M10 propellant absorption data than 5.7 mm from the surface. Figure 6 illustrates the large attenuation of the incident light. This broadband attenuation has been accounted for by a multiplicative term in the absorption equation (Vanderhoff, Anderson, and Kotlar 1992; Vanderhoff, Teague, and Kotlar 1992) that is a power series which includes four coefficients that are allowed to vary to approximate the baseline.

Many of these absorption spectra are obtained as a function of distance from the surface for each propellant burn experiment. Dark zone temperature and NO mole fraction values for M10 propellant obtained from a least-squares fitting procedure are shown in Figures 7–10. Different symbols are used to denote data taken at different pressures. The dark zone temperatures for the higher pressures are shown on Figure 7 and the two lower pressures are shown on Figure 8. The video records show that the dark zone was not well defined for many of the M10 propellant burns (i.e., the luminous flame attached and detached from the surface in a random fashion). At the lowest pressure the luminous flame did not appear. In addition to the variable position of the luminous flame, this propellant produced enough soot to interfere with the optical measurements. Considering these variables, it is not surprising to find substantial scatter in the M10 propellant data. The results of Figure 8 indicate a dropping temperature as the distance from the propellant increases. Here the luminous flame does not establish itself and

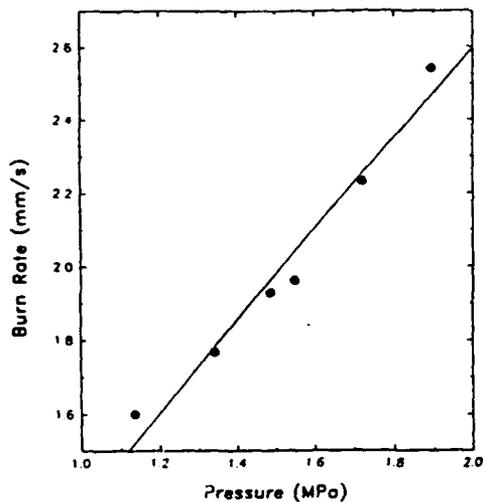


Figure 3. Burn rate of M10 propellant vs. nitrogen buffer gas. An exponential fit gives $n = 0.95 \pm 0.09$ and $a = 1.35 \pm 0.06$.

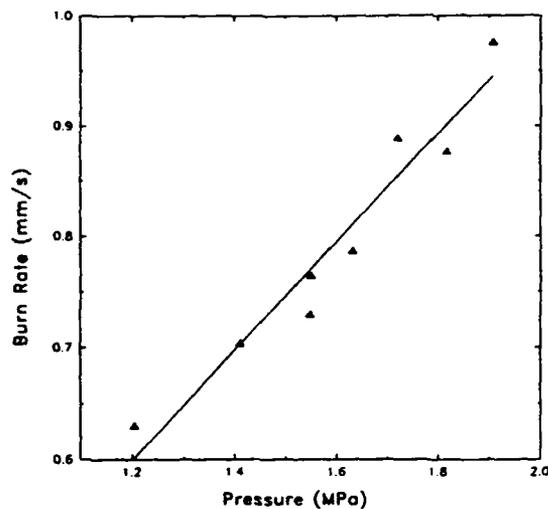


Figure 4. Burn rate of XM39 propellant vs. nitrogen buffer gas pressure. An exponential fit gives $n = 0.98 \pm 0.11$ and $a = 0.50 \pm 0.03$.

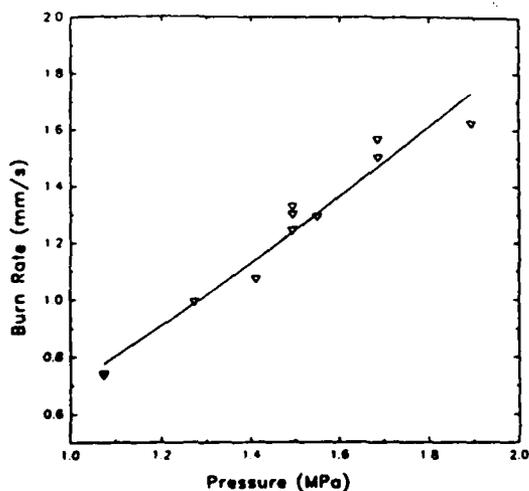


Figure 5. Burn rate of M43 propellant vs. nitrogen buffer gas pressure. An exponential fit gives $n = 1.41 \pm 0.11$ and $a = 0.70 \pm 0.04$.

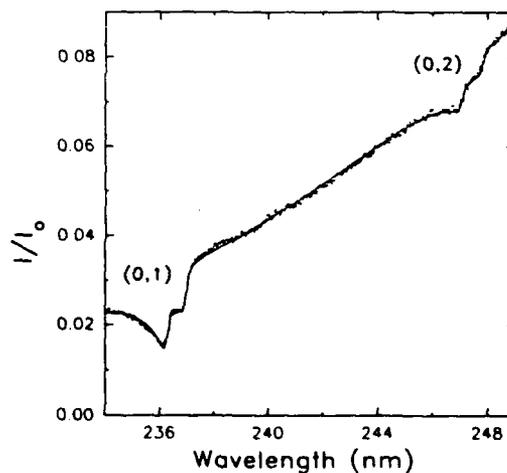


Figure 6. Absorption spectrum of NO taken in the dark zone region of M10 propellant burning at a pressure of 1.9 MPa. The two hot bands are labelled.

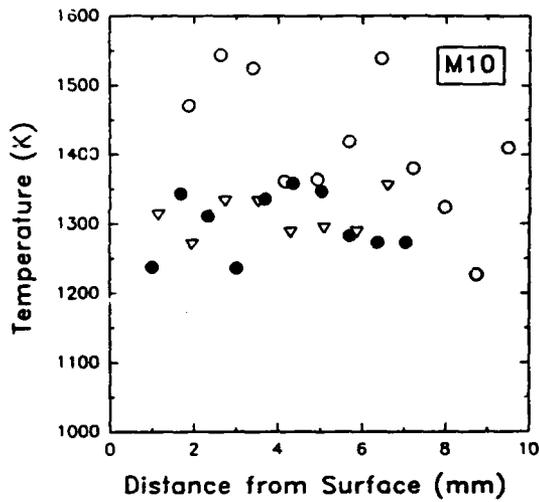


Figure 7. Gas phase temperatures as a function of distance from the propellant surface for M10. The open circles are for 1.89 MPa, filled circles 1.72 MPa, and open triangles 1.55 MPa nitrogen gas pressure.

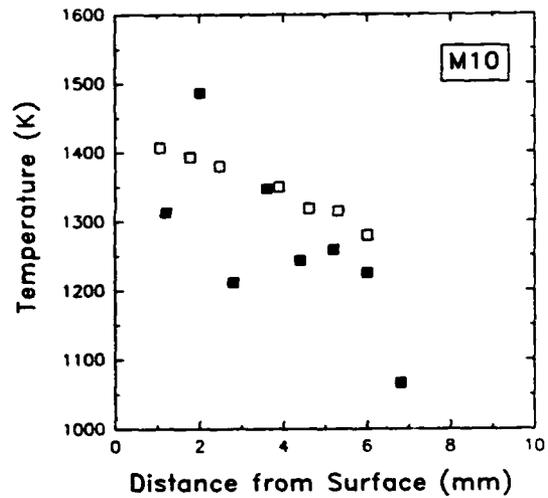


Figure 8. Gas phase temperature as a function of distance from the propellant surface for M10 propellant. The filled squares are for 1.13 MPa, and the open squares represent 1.34 MPa nitrogen gas pressure.

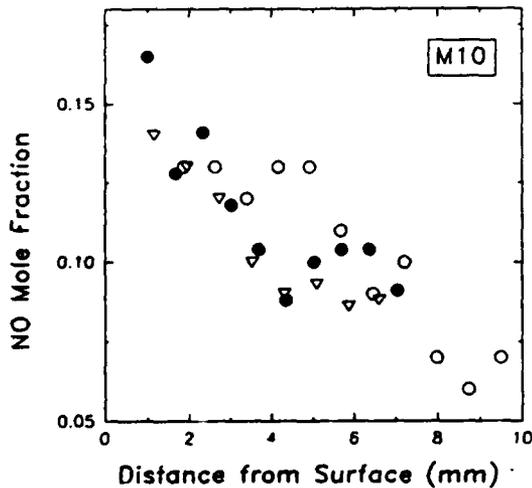


Figure 9. Mole fraction of NO vs. distance from the M10 propellant surface. The symbols are for the same nitrogen pressures as in Figure 7.

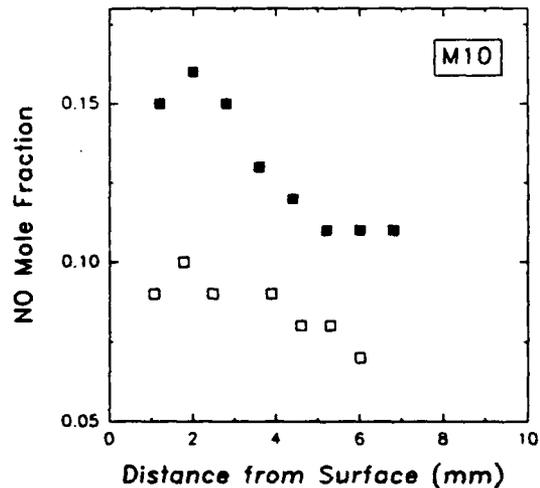


Figure 10. Mole fraction NO vs. distance from the M10 propellant surface. The symbols are for the same nitrogen gas pressures as in Figure 8.

is expected with distance from the propellant surface. Although the temperature range is from about 1,250 to 1,550 K, most of the experimental data fall in the range from 1,250 to 1,400 K and we estimate the dark zone temperature for M10 to be $1,325 \pm 75$ K.

NO absorption spectra have also been obtained for two RDX nitramine propellants, XM39 and M43. These propellants have been designed for low vulnerability and they burn rather poorly at low pressure; thus, there is appreciable scatter for these measurements. Gas phase temperatures for XM39 propellant as a function of distance from the propellant surface are shown on Figures 11 and 12. The dark zone temperatures for XM39 mostly fall between 1,100 and 1,400 K, where the lower pressure data of Figure 12 give the lower temperatures. Our estimate of the dark zone temperature for XM39 propellant is $1,275 \pm 75$ K. The NO concentrations are given in Figures 13 and 14 and range in value from about 0.12 to 0.18. The lower pressure data indicates higher NO concentrations. Our estimate for the NO fraction in the dark zone of XM39 propellant is 0.15 ± 0.02 .

Temperatures ranging from about 1,050 to 1,450 K are obtained for the M43 propellant (see Figure 15) and our estimate for the dark zone temperature is $1,200 \pm 100$ K. The NO mole fractions for M43 are displayed in Figure 16 and range from about 0.12 to 0.30. However, most of the values fall within a tighter range, and our estimate for the NO mole fraction is 0.22 ± 0.03 .

4. DISCUSSION

In the last section, estimates for propellant dark zone temperatures and NO concentrations have been given. How these values compare to other published data and how they relate to energy conservation will be discussed in this section.

Comparisons of present data with other published data are given in Tables 2 and 3 for single-base and nitramine propellants, respectively. No published data for dark zone temperatures and NO concentrations have been found for single-base propellants. Thus, the comparison in Table 2 is between single-base and double-base propellants. Four double-base propellants are shown for comparison, and the final equilibrium temperatures for these propellants are also given in the last column. The equilibrium temperature has been calculated from the NASA-Lewis thermochemical equilibrium code (Svehla and McBride 1973) and provides a basis for ordering these propellants. The ordering follows from the fact that these propellants burn rich; thus, the final flame temperature is strongly dependent on the dark zone temperature and the

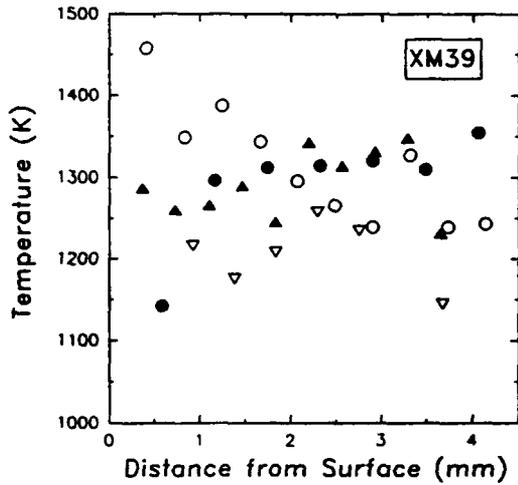


Figure 11. Gas temperature as a function of distance from the XM39 propellant surface. The open circles and filled circles are for 1.72 MPa, filled triangles 1.82 MPa and open triangles 1.63 MPa.

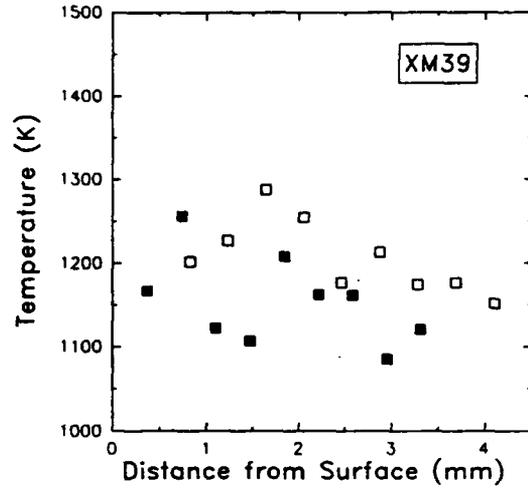


Figure 12. Gas phase temperatures as a function of distance from the XM39 propellant surface. The open squares are for a pressure of 1.41 MPa and the filled squares are for 1.20 MPa.

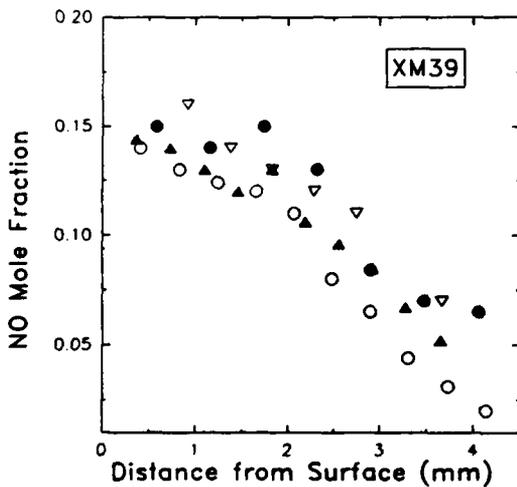


Figure 13. Mole fraction NO vs. distance from the XM39 propellant surface. The symbols denote the same nitrogen buffer gas pressures as in Figure 11.

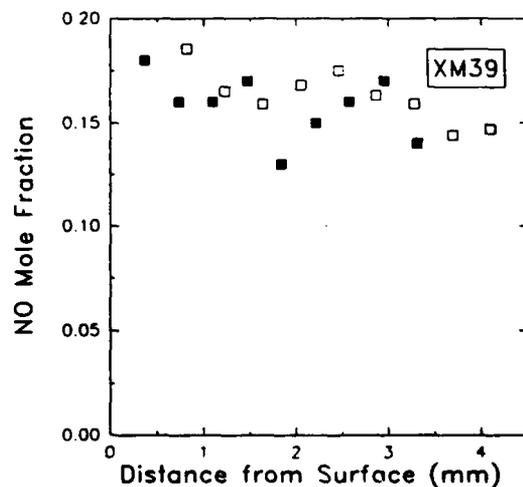


Figure 14. Mole fraction NO vs. distance from the XM39 propellant surface. The symbols denote the same pressures as in Figure 12.

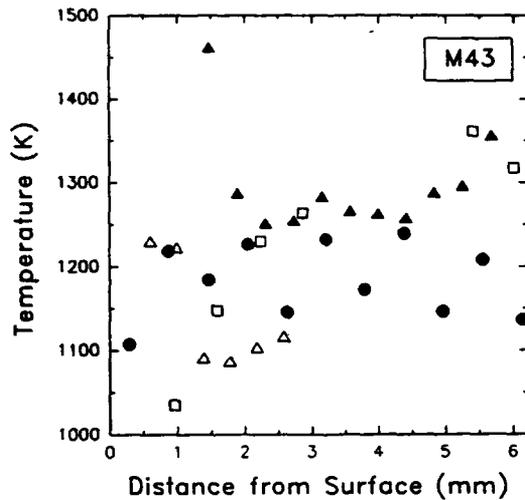


Figure 15. Temperature as a function of distance from the M43 propellant surface. The filled circles are for 1.1 MPa, the open and filled triangles 1.27 MPa and the open square 1.47 MPa.

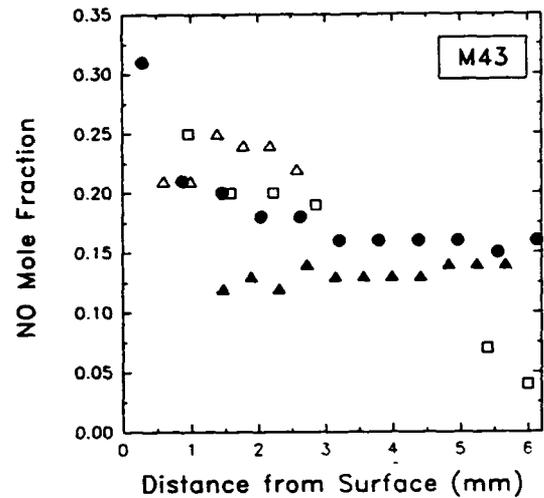


Figure 16. Mole fraction NO vs. distance from the M43 propellant surface. The filled circle is for 1.1 MPa, open triangle and filled triangle 1.27 MPa and open square 1.47 MPa.

Table 2. Comparison of Dark Zone Temperatures, NO Mole Fractions and Final Equilibrium Temperatures for Single- and Double-Base Solid Propellants

Propellant	Reference	Dark Zone Temperature (K)	NO Fraction	Equilibrium Temperature (K)
M10	Present Data	1,325	0.145	2,585
JA2 ^a	A	1,450	0.24	2,793
DB1 ^a	B	1,500	0.21	2,813
M9 ^a	A	1,500	0.30	3,023
DB2 ^a	C	1,600	0.24	3,076

^a Propellant compositions are given in the Appendix.
 Notes: A - see Vanderhoff et al. (1992a, 1992b).
 B - see Lengelle et al. (1984).
 C - see Heller and Gordon (1955).

Table 3. Comparison of Dark Zone Temperatures, NO Mole Fractions, and Final Equilibrium Temperatures for Solid Nitramine Propellants

Propellant	Reference	Dark Zone Temperature (K)	NO Fraction	Equilibrium Temperature (K)
HMX-PE ^a	D	1,300	0.17	1,928
HMX2 ^a	A	1,310	0.13	2,080
XM39	Present Data	1,275	0.15	2,354
M43	Present Data	1,200	0.22	2,452

^a Propellant compositions are given in the Appendix.

Notes: A - see Vanderhoff et al. (1992a, 1992b).

D - see Kubota (1982).

amount of oxidizer left to be consumed. The only oxidizer which is far in excess of the equilibrium value is NO; thus, the temperature increase from the dark zone to the luminous flame is dependent primarily on the amount of NO present in the dark zone. M10 propellant has the lowest final flame temperature and the lowest NO fraction, which is consistent with the ordering scheme. M43 has the highest flame temperature for the nitramines comparison and has the highest NO mole fraction in the dark zone. XM39 is intermediate in final flame temperature and has an intermediate NO mole fraction. All of the measured dark zone temperatures for nitramine propellants are within about 100 K of each other.

5. SUMMARY

From the video records, low pressure burn rates have been measured for M10, XM39, and M43 solid propellants. Absorption spectroscopy of the NO molecule provided the means to obtain dark zone temperatures and NO concentrations for these propellants as both a function of pressure and distance from the propellant surface. Although no published data were found for a direct comparison, the present data correlate well with data on similar propellants.

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APPENDIX:
PROPELLANT COMPOSITION FOR VARIOUS SOLID PROPELLANTS

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Table A-1. Ingredients and Composition for Various Solid Propellants

Propellant	Ingredient	Weight (%)
JA2	Nitrocellulose (13.04% N)	58.2
	Nitroglycerin	15.8
	DEGDN ^a	25.2
	AKARDIT II	0.05
M9	Nitrocellulose (13.29% N)	57.6
	Nitroglycerin	40.02
	Ethyl Centralite	0.73
	Potassium Nitrate	1.63
DB1	Nitrocellulose (11.6% N)	52
	Nitroglycerin	43
	Ethyl Centralite	3
DB2	Nitrocellulose (12.6% N)	55
	Nitroglycerin	45
HMX2	HMX ^b	80
	Binder 1 ^c	20
HMX-PE	HMX	80
	Binder 2 ^d	20

^a Diethylene Glycol Dinitrate

^b Cyclotetramethylenetetranitramine

^c Polyester Binder

^d Polyether Binder

NOTE: The nitration level N is also given for the nitrocellulose.

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