A Study of Composite Solid-Propellant Flame Structure Using a Spectral Radiation Shadowgraph Technique

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This study elucidates the fine-scale structure of composite propellants in the vicinity of the burning surface. An experimental approach to the problem of analyzing flame structure based on measurements of flame radiation is presented. The technique was to burn propellant strands backlighted with a mercury light and to record simultaneously the spectra of flame gases and mercury light. The cutoff of the mercury light by the unburned portion of the strand indicates the location of the propellant surface on the recording photographic plate. Comparison of the position of onset of flame species relative to the onset of mercury emission yielded spatial resolution of the species relative to the propellant surface. It was concluded from microdensitometer scannings that the CN emission at 3883 Å begins slightly above the burning surface, at a distance of approximately 70 μ and persists over a region of about 2 mm (width at 50% peak intensity). Peak CN radiation was found to occur at a distance of less than 235 μ from the propellant surface. Spectra obtained at pressures above atmospheric revealed a strong continuum that obscured the CN line to such an extent that meaningful measurements were not possible.

Introduction

A COMPLETE understanding of composite solid-propellant burning, be it steady or oscillatory in nature, will never be available until the region adjacent to the burning surface can be probed in minute detail. An understanding of the decomposition is complicated by the irregular array of oxidizer crystals, bound together in a heterogeneous fashion by a fuel binder, with attendant microscopic crevices. The advancing flame front, which causes gradients in the order of thousands of degrees per millimeter, may produce thermal stresses and cracking of the multisized oxidizer crystals, adding to the complexity. The multiplicity of binder materials used helps to confuse our limited knowledge regarding the combustion processes. In view of our limited knowledge, theory cannot serve as well as experiment at this stage. Microscopic details are needed regarding physical and chemical structure. There is a need to examine oxidizer-binder interfacial reactions, initial condition of the oxidizer crystal structure, phase changes associated with the binder material, sublimation and reaction of oxidizer and subsequent mixing and diffusive burning, and changes in fuel pyrolysis or polymerization processes due to changing oxidizer particle size.

This study has as its ultimate objective the elucidation of the fine-scale structure of a typical composite propellant flame in the vicinity of the burning surface. The experimental technique is presented in this paper as well as the results with the CN (violet) radiation. The initial experiments were performed with CN because this species is formed only from a reaction between the binder and oxidizer for the propellant used herein. Also, the CN radiation in some premixed flames has been shown to be confined almost completely to the reaction zone with only weak extensions into the burnt gas.[1] The spatial resolution of various flame species is discussed in Ref. 2 for both premixed and diffusion type flames. In a diffusion flame each band has a definite position within a thick reaction zone whereas in a premixed flame all the bands are emitted from about the same position in a rather narrow reaction zone. Reference 3 shows that the C_2, CH, CN, and NO emission of premixed flames with nitrous oxide is limited to a narrow reaction zone with the maximum intensity occurring with slightly fuel rich mixtures. The relation of the luminous flame zone to the temperature and oxygen concentration has also been investigated, see Refs. 2 (p. 130) and 4.

Basically, the technique used herein was to burn propellant strands backlighted with a mercury light source and to simultaneously record the spectra of flame gases and mercury light using a high aperture spectrograph. The cutoff of the mercury light by the unburned portion of the propellant strand indicated the location of the propellant surface on the recording photographic plate. By careful comparison of the position of onset for the flame species with the onset point for the mercury light, it was possible to obtain spatial resolution of the species relative to the propellant surface. In this manner it is possible to map out the regions or zones wherein the various flame species emit, as well as obtain, their emission profiles. This information could then be used to infer flame zone structure and hence to determine the validity of reaction sequences such as ammonium perchlorate decomposition followed by an oxidizer-binder vapor diffusion flame.

Experimental Technique

The optical arrangement is shown in Fig. 1a. The image of the mercury arc was focused on a strand of polybutadiene-acrylic acid, ammonium perchlorate propellant (PBAA-AP) 1 in. high by $\frac{1}{2}$ in. wide by $\frac{1}{8}$ in. thick as shown in Fig. 1b. The propellant was composed of 78%-by-weight ammonium perchlorate whose mean weight diameter was 11 μ. The propellant strand and mercury image were then focused on the slit of an f/6.3 anastigmatic spectrograph whose reciprocal dispersion is 20Å/mm. The image of the mercury light was sufficiently large to cover the slit of the spectrograph in the absence of the propellant strand. The neutral density filters were used to attenuate the mercury light source to obtain equality between flame spectra and mercury line intensities. The optical lengths shown in Fig. 1a are given to the nearest inch.

Recording of the simultaneous spectra of mercury light and flame gases was made photographically by using a 200-μ slit opening on the spectrograph and an exposure time of 1 sec corresponding to a movement of the propellant surface of approximately 1.5 mm. Exposures were made when the propellant surface was centered about the optical axis. Various emulsions were used to photograph the spectra with

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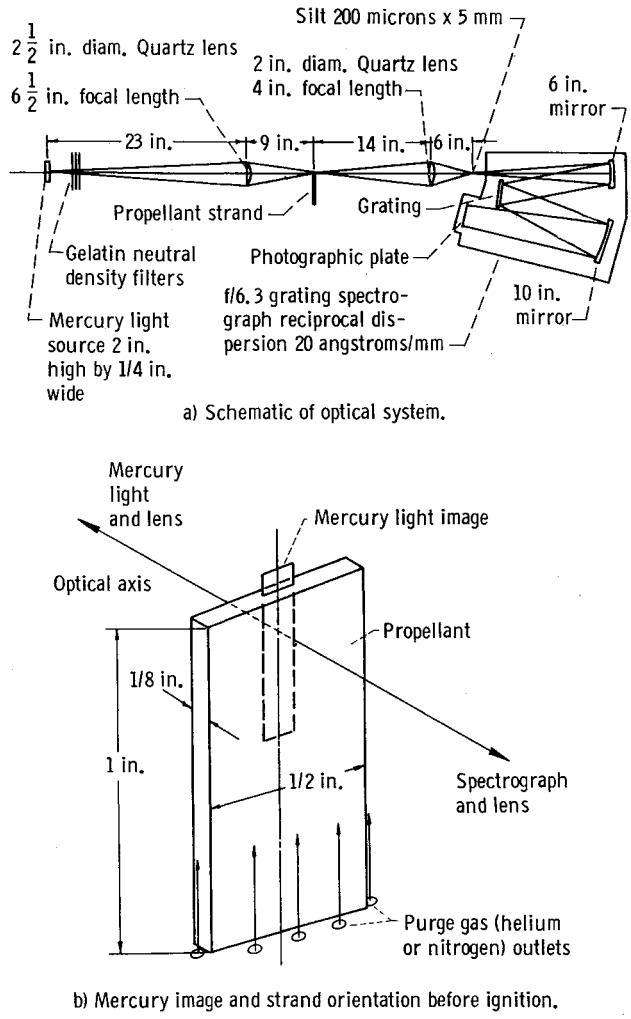

Fig. 1 Optical system for obtaining spatial resolution of flame gas species.

the majority of the results being recorded on Kodak spectroscopic plates (types I-O and I-F) that had high sensitivity coupled with acceptable resolving power and contrast. The emulsion sensitivities extended over a range from 2800 to 5000 Å and 2800 to 7000 Å, respectively.

The propellant was ignited by a nichrome ribbon $\frac{1}{8}$ in. wide and several thousandths of an inch thick. The ribbon made contact with the entire upper surface of the propellant and was maintained in tension while being resistance-heated with a 10-v battery. Ignition occurred uniformly over the propellant surface. All faces of the strand were freshly cut, and no inhibiter was used.

Trial and error regulation of the upward flowing purge gas (helium or nitrogen, Fig. 1b) established the amount of flow necessary to prevent both side burning, which would lead to a convex surface, and decreased edge burning, which would lead to a concave surface.

Spectra of PBAA-AP strands were obtained at pressures up to 800 psi by using a vented bomb system. The data were reduced by using a recording microdensitometer that had a maximum resolution of 1μ. Spectral line densities from both the flame gases (CN violet band head at 3883 Å) and mercury light, as well as their respective backgrounds, were recorded at $\times 50$ by the microdensitometer as a function of vertical distance (constant wavelength) on the photographic plate. The pen-displacement record obtained from the microphotometer was linear with density as shown in Fig. 2a. The density (or displacement) profiles were converted into intensity profiles by using a calibration curve (Fig. 2b), which was obtained by varying the exposure time

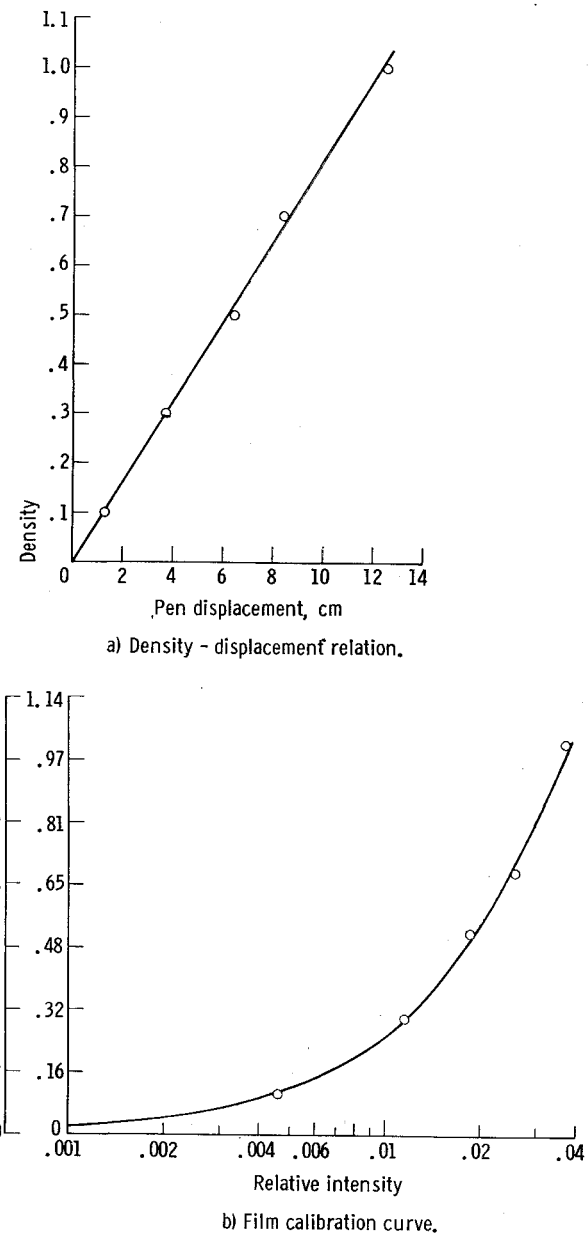

Fig. 2 Microdensitometer and film calibration.

of the mercury light source. The background intensity was then subtracted from the sum of the line and the background intensity. The resulting intensity profiles for the CN and Hg line were then superimposed to determine the position of the flame spectra onset. Because of the coarse granularity of the film emulsion some difficulty was experienced in specifying the threshold point at which the line intensity started to rise. It was convenient, therefore, to use the 50% point of maximum intensity for each profile in order to determine CN emission onset relative to the Hg line. It is estimated that this technique yielded a result which was within $\pm 20\%$ of the value obtained from the threshold point.

Results and Discussion

General Radiation Characteristics

The general ultraviolet and visible radiation characteristics of the PBAA-AP propellant at atmospheric pressure are shown in Fig. 3 and consist primarily of OH, NH, CN, and CH. Spectra of PBAA-AP propellants have been published previously.[5]

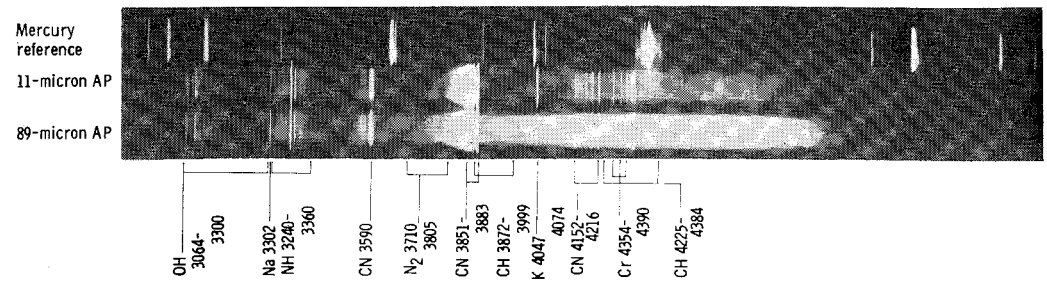

Fig. 3 Spectra of burning propellant PBAA-NH_4ClO_4 125 μ slit, 1 sec exposure.

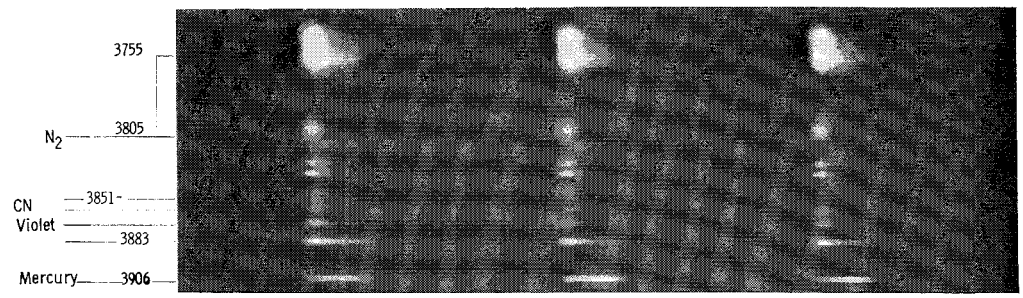

Fig. 4 Spectral radiation lines analyzed.

Onset of Emission

A narrow region of the spectra obtained at atmospheric pressure with the backlighted strands is shown in Fig. 4. The height of the CN line was controlled by the magnification of the image on the spectrographic slit. In Fig. 4 the magnification was 1/2.36. Microphotometer scanning of the CN and Hg lines and their respective backgrounds adjacent to the lines yielded the density profiles shown in Figs. 5a and 5b. These density profiles were converted into intensity profiles by means of Fig. 2b. Subtraction of the background radiation from the line-plus-background for both CN and Hg yielded the final curves for comparison (Fig. 6a). The point of CN emission onset relative to the Hg line was determined by using the 50% point of maximum intensity for each profile as shown in Fig. 6a. In this particular example, the onset of CN begins prior to the onset of Hg by an amount δ_1 equal to 335 μ. A large number of tests showed that the onset of CN emission δ_1 occurred over a range from 445 μ below to 72 μ above the mercury; the latter case is shown in Fig. 6b. The majority of the measurements indicated CN emission occurred prior to the Hg onset with only a small percentage of the results showing Hg onset prior to that of CN. Although the propellant surface could be maintained level before ignition, burning is believed to occur with a small degree of surface tilting. Sloping of the burning either toward or away from the slit of the spectrograph to approximately $\frac{1}{64}$ in. could explain the range of values observed. If the surface was tilted toward the slit, comparison of the spectral lines of CN and mercury would have shown the onset of CN emission before that of the mercury. With the opposite slope, the CN onset position would occur close to the mercury onset position; with a level surface, the CN would be at some point above the mercury. Tests, performed with a definite slope of the surface toward the slit, showed CN emission much below the mercury. The maximum value above the mercury would therefore represent the position where the species CN first began to appear. That value is 72 μ above the decomposing surface.

Some data were obtained when the propellant surface was centered either above or below the optical axis. The range of values observed did not exceed those cited previously. These data, however, are not conclusive in light of surface tilting during burning.

Refraction Effect

The mercury light passes through a region of varying gas density as it traverses the flame gases. It experiences, therefore, a refraction effect toward the propellant surface (Fig. 7) because the gas temperature increases rapidly from ~1000°F (surface temperature) to ~4000°F (flame temperature). When planar flow $dT/dx = 0$ is assumed, it is possible to calculate the amount of deflection of the emerging light ray by using the relationship[6]

$$\epsilon = (X_1\beta/\rho_s)(d\rho/dy)$$

where β is defined from the expression

$$n = 1 + \beta(\rho/\rho_s)$$

n is the index of refraction and ρ_s is the reference density.

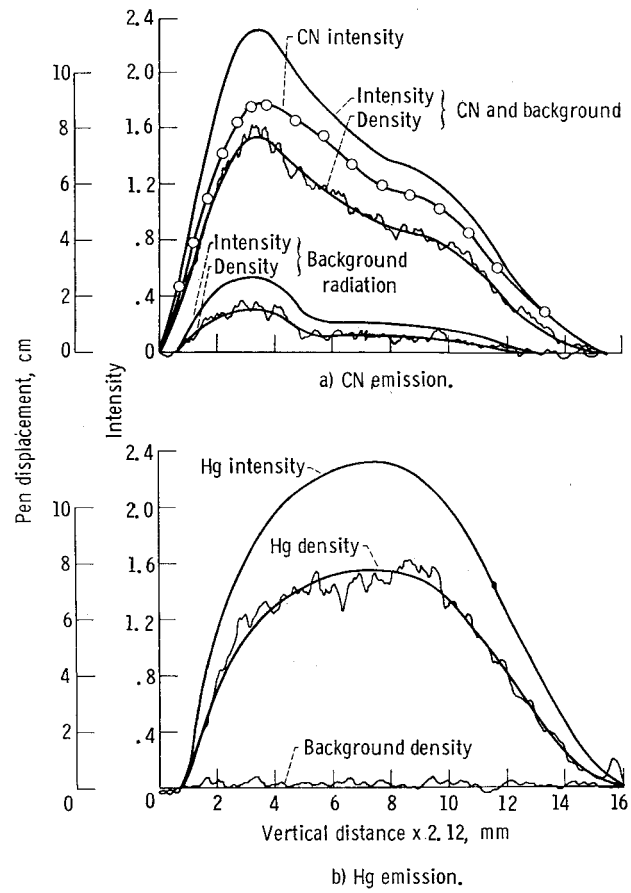

Fig. 5 Intensity profiles.

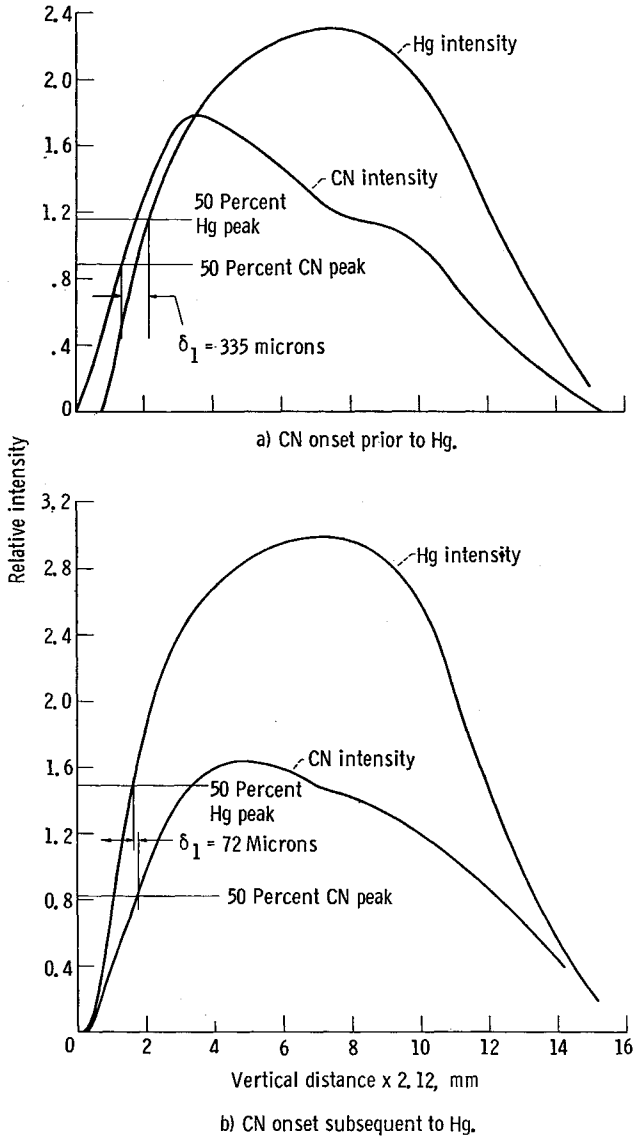

Fig. 6 Comparison of CN and Hg intensity profiles.

The following values were used to estimate ϵ: X_1 path length, 3000 μ; β density ratio coefficient for air, 0.00029; ρ_s standard air density, 0.075 lb/ft^3; and $d\rho/dy \approx 1.9(10)^{-2}/200$, corresponding to a temperature change of 3000°F over a 200 μ range. This yields a value of $\epsilon = 0.00105$ rad; δ_2 (see Fig. 7) is given by $\delta_2 = X_1 \tan\epsilon = 3\mu$. The CN emission therefore occurs at approximately 70 μ above the surface if the mercury light refraction is considered.

Secondary Reaction

The double-peaked profile obtained from the CN emission indicated the possibility of several distinct reaction zones, analogous to the well-known flame structure of double-base propellants. It was finally suspected, however, that the purge system used in the present experiments did not exclude the possibility of air entrainment in the flame gases followed by further reaction of the fuel-rich gases with the entrained air. Subsequent experiments were run in a chamber with quartz windows from which the air was purged with nitrogen. The resulting CN profile is shown in Fig. 8, a clear demonstration of an entrainment effect causing subsequent reaction in the exhaust stream.

CN Zone Thickness

The distance $\mathcal{L}$ over which the CN species emits may be determined by using the line profile shown in Fig. 8. In

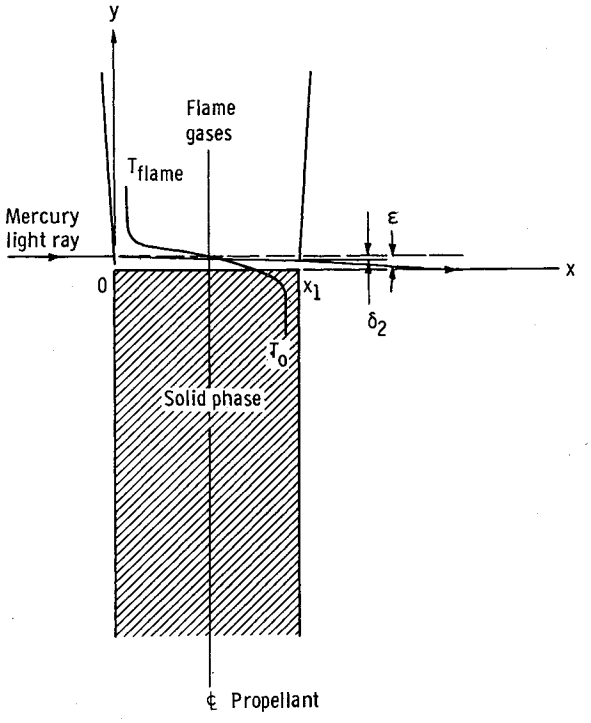

Fig. 7 Refraction of mercury light passing through flame gases.

order to do so, it is necessary to correct the profile by the amount that the surface recedes during t, the time of film exposure, that is,

$$\mathcal{L} = L - tr$$

where r is the linear regression rate and L is the uncorrected profile length. Since the CN profile decays slowly in the upstream direction, the 50% point was taken as being representative of the zone thickness. This persistence of the CN into the burned gases may be because the propellant composition is slightly fuel rich. For very rich premixed flames it has been observed that the C_2 and CN molecules formed in the reaction zone may have an unusually long lifetime and persist in the burned gases.[3] Measurements of L at the 50% intensity point, as in Fig. 8, indicate a value of 3.5 mm when the exposure time is 1 sec and the burning rate is 0.06 in./sec. This leads to a CN zone thickness of

$$\mathcal{L} = 3.5 - 1.5 = 2.0 \text{ mm}$$

That is, CN emits over a region 2 mm in thickness. This

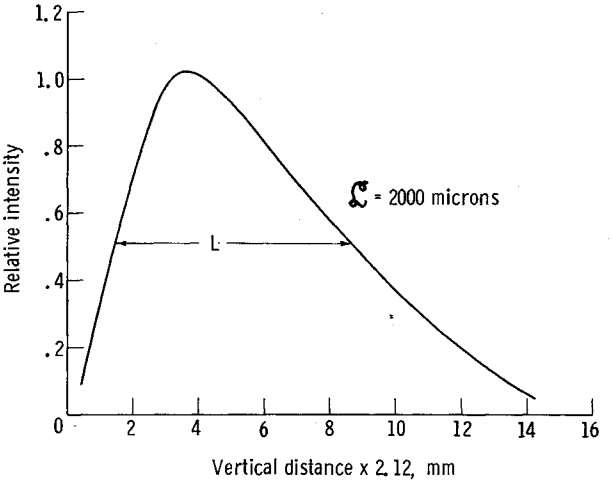

Fig. 8 CN Intensity profile with no secondary reaction.

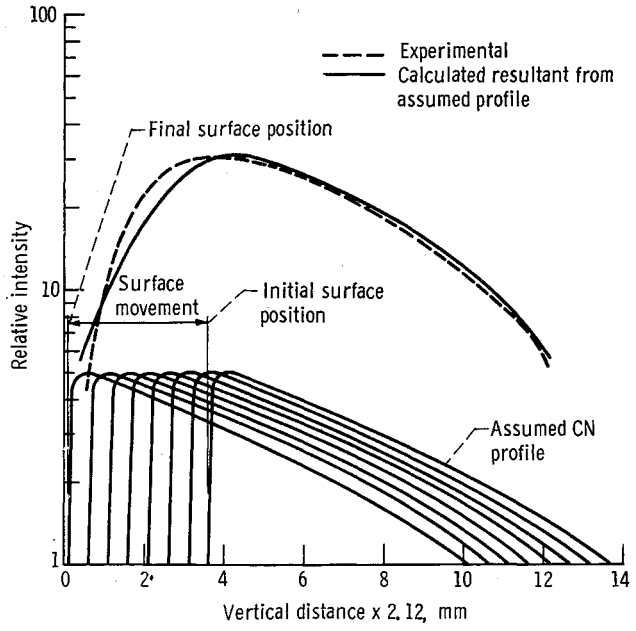

Fig. 9 Comparison of experimental and calculated CN profiles.

region has its beginning slightly above the solid propellant-surface, that is 70 μ.

The correction of the CN profile in the preceding paragraph does not, however, yield any information regarding the actual line profile or its position of maximum radiation because of the surface regression during the time of exposure. The effect of the surface movement is to give an emission profile that is integrated over distance (or time). In order to determine the actual profile and the position of peak CN radiation relative to the propellant surface, a trial and error technique was employed on the CN line shape and thickness. This profile was assumed to be invariant with time and was repeated at eight equally-spaced intervals as shown in Fig. 9. The extreme positions of the profile were placed to correspond to the distance moved by the propellant surface during the exposure time. Summation of the radiative effect from the eight profiles yielded a resultant curve for comparison with the experimentally observed curve. Various line shapes (slope of rising and decaying portions and peak position) and thicknesses were tried. The best fit was obtained with the profile shown in Fig. 9. The exact profile might be obtainable by suitable differentiation of the observed profile. Peak CN radiation of the assumed profile is seen to occur at $\frac{1}{10}$ the distance to the resultant peak. Also shown in Fig. 9 is the experimentally observed profile, which is replotted from Fig. 8. Since the calculated profile does not coincide exactly with the experimental profile, it was concluded that the peak CN radiation occurred at less than $\frac{1}{10}$ the observed value, that is, 165 μ. The analysis of the data does not allow for a more specific value, and it is possible that the peak CN radiation approaches much closer to the propellant surface. The distance $\mathfrak{L}$ over the CN emits is 2 mm as measured from the assumed profile. This is in agreement with the value determined in the preceding paragraph.

Previous measurements,[7] based on the use of fine thermocouples embedded in the propellant or a brightness-emissivity technique, have indicated that the adiabatic flame temperature is reached at a distance of less than 100 μ from the surface (50–800 psig). On the basis of these measurements the authors concluded that the gaseous reaction zone thickness was of the order of 100 to 200 μ. However, later measurements, based on the CO_2 radiation, showed that the adiabatic flame temperature is reached at 0.8 mm above the propellant surface and it was concluded, therefore, that the reaction zone is 800 μ in thickness at a combustion pressure of 800 psig.[8] This result is in closer agreement with the value reported in the present work if it is assumed that the CN emission is confined to the reaction zone with only weak extensions into the burned gas. The difference between the 0.8 mm, reported in Ref. 8, and the 2 mm reported in the present work may be due to a pressure effect. The possibility of CN radiation being linked to solid particle decomposition in the gas stream has been considered, but no particles were observed in the gas stream. The measurements from the present experiment indicate a flame zone thickness that is nearly 20 times thicker than reported previously[7] and is indicative of a distributed reaction zone above the decomposing solid surface.

Spectra from Pressurized Combustion

Figures 10a and 10b show spectra obtained at combustion pressures of 50 and 100 psi, by using a double window vented burner. The increased intensity of the carbon continuum obscures the CN line to such an extent that meaningful measurements are not possible. The same difficulty had been experienced previously[9] with this propellant in attempting to photograph the burning surface through the flame gases. Some success has been reported[10] in eliminating flame opaqueness by using polyurethane binder with ammonium perchlorate *AP*. Preliminary results obtained in the present study with polyurethane propellant showed only a faint continuum with some OH and NH lines present in addition to sodium.

Summary of Results

An experimental technique, utilizing the onset of flame species radiation relative to the onset of a background mercury source yielded a means for obtaining the spatial resolution of various species above the burning solid-propellant surface. Microdensitometric scanning of the photographed spectra revealed that the onset of CN radiation at 3883 Å occurred over a range extending from 445 μ below to 72 μ above the mercury. It was reasoned that the propellant burned with a small degree of surface tilting either toward or away from the spectrograph slit. Tilting or sloping of the surface to $\frac{1}{64}$ in. could explain the range of values obtained. It was concluded that the position of CN onset is given by the maximum value above the surface, namely, 72

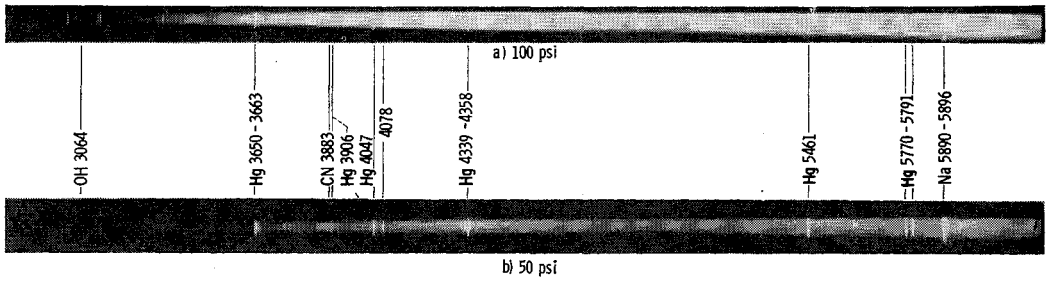

Fig. 10 Spectra of burning propellant: 50 μ slit; exposure, ½ second; film type, Eastman I-F.

μ. Consideration of the refraction effect of the mercury light as it passes through the flame gases revealed a correction of 3 μ. The CN intensity profile, corrected for surface movement, showed that CN emission persisted over a region of approximately 2000 μ (width at 50% peak intensity). Peak CN radiation was found to occur at a distance of less than 235 μ from the propellant surface.

Spectra obtained at pressures above atmospheric pressure revealed a strong continuum which obscured the CN line to such an extent that meaningful measurements were not possible.

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