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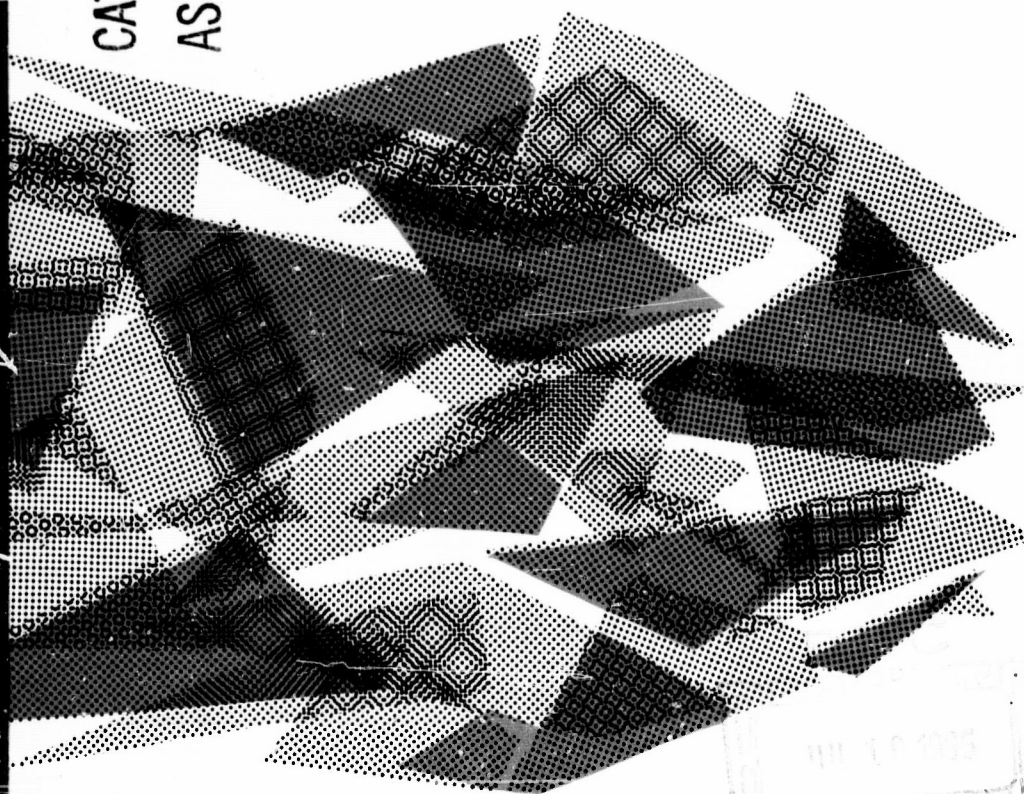
REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

SPECIAL REPORT NO. S-75

A SPECTROGRAPHIC TECHNIQUE FOR THE
STUDY OF SOLID PROPELLANT COMBUSTION (U)

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REDSTONE ARSENAL RESEARCH DIVISION
HUNTSVILLE, ALABAMA

REPORT NO. S-75

A SPECTROGRAPHIC TECHNIQUE FOR THE STUDY OF
SOLID PROPELLANT COMBUSTION

By

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Contract Numbers:

DA-01-021 AMC-11,536(Z)
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July 15, 1965

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NOTE ON CLASSIFICATION

The entire contents of this report are Unclassified with the single exception of Table I, page 15.

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HUNTSVILLE, ALABAMA

ABSTRACT

A micro window bomb has been modified for use with a grating spectrograph to observe the flame zone of deflagrating solid propellant with the aim of identifying transient species, their emergence, and their spatial distribution in the flame. Qualitative contrasts between fuel-binder, plastisol-nitrocellulose and NF-binder composite formulations are reported. Prior literature is reviewed in detail.

ACKNOWLEDGMENTS

The carboxy-terminated and plastisol-nitrocellulose composite propellants were provided by Mr. James L. Chaille and, Mr. Stanley E. Anderson. The NF-containing propellants were supplied by Mr. Paul H. Gehlhaus.

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A SPECTROGRAPHIC TECHNIQUE FOR THE STUDY OF SOLID PROPELLANT COMBUSTION

INTRODUCTION

In the past decade, the solid-propellant industry has seen significant improvement in suppression of combustion instability, control of burning rates, and attainment of higher impulses, largely because of the resourcefulness of workers in the field at finding a "quick-fix." However, the very success of "quick-fixes" has led to a neglect of the fundamentals of solid propellant combustion, and such neglect can become serious when the usual remedies no longer work. For example, one deterrent to a fundamental attack on the problems of unsteady burning has been the lack of basic knowledge of the way in which a composite propellant burns under steady-state conditions. As a result, the need for basic research in solid propellant combustion has become more urgent, and several investigators are now studying the details of the combustion mechanism.

In planning such a study the researcher must first decide on which aspect of combustion he will concentrate, since realistic considerations dictate that some narrowing of the field must be made for any meaningful work to be accomplished. In the work to be described, attention has been focussed on the gaseous region of the combustion wave.

BACKGROUND

The structure of the gaseous region in the solid propellant reaction zone needs to be studied and clarified for a number of reasons. Among these are (a) determination of the causes of inefficient combustion, where the full energy available is not attained inside the motor chamber, probably because of reactions which require times long compared to the residence time in the chamber, (b) locating the rate-controlling steps in the several reactions and observing the importance of diffusion of active species as a rate-limiting factor, and (c) finding the extent of the zone, with particular reference to obtaining theoretical models which could provide a feedback to predicting methods by which the regression rate can be influenced for a wide range of variables.

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Optical methods are preferable for the investigation of this structure, for two main reasons. First, they have the advantage of remoteness; no foreign body need be introduced into the reaction zone with an unknown amount of catalysis or gas flow disruption occurring. Second, they have greater spatial resolution. Mechanical-probe techniques are limited by the small thickness of the gaseous reaction zone. For composite propellants, estimates of the extent of the zone range from 50 microns to about 2 millimeters.

It is well, at this juncture, to discuss the question of thickness in some detail. In some of the original work on composite propellant flame zone structure, Sutherland (1) used a variety of techniques - spectrographic, thermocouple, and brightness-emissivity - and was led to the conclusion that the flame temperature was reached within 50 microns from the burning surface for an ammonium perchlorate-polystyrene propellant. There was some spectrographic indication that the reaction zone extended to 500 microns from the surface. However, Penzias and Tourin (2), using infrared radiometry, found that a poly(vinyl chloride)-ammonium perchlorate propellant burning at 800 psi did not attain the adiabatic flame temperature until almost 1 millimeter from the surface. Povinelli (3), using spectrographic techniques to be discussed later, found maximum reaction intensity at about 250 microns from the surface of an ammonium perchlorate-polybutadiene-acrylic acid propellant burning at atmospheric pressure, and also observed a large amount of radiation emitted at 2 millimeters from the surface. Sabadell (4) used fine ($<10\mu$) thermocouples to investigate the thermal profile (mainly in the solid phase). It was observed that an apparent temperature plateau existed, since, after the initial steep rise, the recorded temperature levelled off at a value below the melting point of the thermocouple wires (platinum/platinum-rhodium) and held this value for about 2 millimeters at 1000 psi. Thus, although a linear thermal gradient characteristic of a flame zone thinner than 100 microns might exist near the surface, this gradient might result from a primary reaction zone, with a diffuse afterburning zone where the reactions go to completion.

It is obvious from this small compendium of conflicting experimental results that more fundamental knowledge of the gaseous reactions is required. One possible method for obtaining this knowledge while retaining the previously mentioned advantages of optical techniques is the use of emission spectroscopy. A large number of references are available which deal with the study of gaseous flames by spectroscopic techniques, some of which are summarized, for instance, in books by Gaydon and others (5) and by Mavrodineanu and Boiteaux (6).

APPROACH

The application of the spectrographic technique is based on the premise that the extent of the reaction zone in the deflagration wave is indicated by the spatial distribution of transient emitters which occur only in such zones. Although the emitters in the ultraviolet and visible regions of the characteristic spectrum represent only a small portion of the energy released during the over-all deflagration process, they still give an indication both of the reactions which are taking place and of the location of these reactions. As an example, if chain reactions are important, the chain-breaking and/or chain-branching steps may be determined. Moreover, diffusion of active radicals is known to be important in determining regression rates at intermediate pressures. In addition, slight formulation changes can vary the fuel-oxidizer interaction and bring about a large change in combustion thermochemistry, and changes in the characteristic emitters may be related to the thermochemical variations.

Since a suitable spectrograph was available for short-term loan, a program was set up to examine the feasibility of using emission spectroscopy as a tool for investigating the reaction zone of deflagrating composite solid propellants.

DETAILED REVIEW OF EARLIER WORK

In discussing the spectral results found by earlier investigators, the propellants will be divided into double-base and composite types, although this work will deal with the latter type only. In the interest of completeness, however, the published work with double-base propellants will be mentioned.

Double-Base Propellants

Little success has been found with the use of spectroscopy with double-base propellant deflagration, as pointed out by Sotter (7), who has reviewed much of the earlier attempts. Heath (8) burned cordite at pressures ranging from 400 to 1600 psi, and found no emitters in the "dark zone." Above the dark zone, he observed some potassium as well as the usual sodium impurity. Rekers and Villars (9) used a piston-type apparatus with a strand burner to hold the burning surface fixed spatially, and were able to study the spatial distribution of emitters as a result. They observed the C_2 Swan bands and potassium lines as the strongest emitters, and observed lead oxide bands for platonized propellants. Impurities such as sodium, calcium, calcium oxide, and iron were also found. Rössler (10) burned single-base propellant (nitrocellulose), and found that strong continuum radiation was present, with only impurities detectable above this background. Sotter used both a medium quartz prism instrument and a Raman spectrograph in his study of cordite burning under a pressure range of up to 500 psi. No attempt was made to resolve the various zones of the reaction. Emitters from 14 species were identified, with lead and lead oxide present only for the platonized propellants. The combustion emitters found were carbon, CN (3883 Å, 3862 Å, and 3550 Å band heads), NH (3370 Å), NO (the γ -bands), and OH. The remainder of the emitters were characteristic of the alkali impurities Na, K, Mg, and Ca or their oxides. At atmospheric pressure, a continuum was observed between 3700 Å and 4600 Å, which was tentatively ascribed to the CO + O "glow." Sotter's results led him to conclude that emission spectra gave little help in analyzing the gas-phase combustion zone of double-base propellants, probably because of the complex nature of the gas phase, with most of the energetic reactions occurring in the thin "explosion zone." The presence of a strong continuum at elevated pressures was also a deterrent, as reported by practically all the investigators mentioned. The continuum was ascribed by Heath to glowing carbon particles in the explosion zone, and it was hypothesized that carbon formed by pyrolysis reacted with nitric oxide to trigger the explosion zone.

Fuel-Binder Composite Propellants

The varying nature of deflagration process in composite propellants – where the reactants must diffuse since they are not pre-mixed as in the case of double-base propellants – has led to a different set of results in experiments involving the use of emission spectroscopy. However, as will be seen, the presence of continuum radiation is still a limiting factor for many propellants.

The first reported spectrographic analysis of a burning composite solid propellant was carried out by Sutherland (1), who studied an ammonium perchlorate–polystyrene propellant burning in air. In addition to the impurity emitters from sodium, cobalt, and copper, he found the C₂ Swan bands, a series of CH bands, CN, NH, OH bands and the NO γ -bands. A carbon continuum obscured many of the details above 4000 Å. The spatial distribution of the emitters was intriguing, since the emitters present in the whole flame (e. g., incandescent carbon, sodium, OH, cobalt) filled the spectrograph slit. On the other hand, those emitters characteristic of the reaction zone (i. e., CN, C₂, CH, NH, NO) seemed to be confined to the region adjacent to the burning surface. By comparing these spectra with hydrocarbon flame spectra, Sutherland drew conclusions on the several steps of the reaction, involving both the fuel-binder pyrolysis and the oxidizer decomposition. As mentioned earlier, however, Sutherland's work was performed in air, leading to undetermined diffusive and oxidative effects.

The next work reported was that of Selzer (11), with modifications continuing to the present time (12). Like Sutherland, he observed propellant burning in air. Ammonium perchlorate was used as oxidizer with polyisobutylene and polyurethane binders. Selzer observed OH, CN, and CH emission, as well as other emitters whose identity was less certain, e. g., C₃ and formaldehyde. The latter was thought to be caused by the initial decomposition of the polyisobutylene molecule. Selzer mapped the spatial distribution of the emitters quantitatively, rather than qualitatively, as done by Sutherland, and found that CN, CH, and NH appeared to have maxima at about 1 millimeter from the surface, with 50% point at close to 2 millimeters from the surface. These numbers are higher than those given on a qualitative basis by Sutherland.

In addition, Selzer found that the NH peak occurred before the CN peak, contrary to Sutherland's finding. In any case, the spectra by these two investigators cannot be regarded as complete, since the propellant was not burning in an inert atmosphere.

Still more quantitative work is being carried out by Povinelli (3). He has focussed his attention on the CN violet radiation at 3883 \AA , since, for the propellant used (ammonium perchlorate-PBAA), this emitter comes only from a binder-oxidizer reaction and is found almost exclusively in the reaction zone of gas flames, with very little extension into the burned gases. To obtain an accurate quantitative mapping, a mercury back-light was used to give a reference point for the location of the burning surface. It was found that, for burning under one atmosphere of nitrogen, the CN peak appeared to occur at about 250 microns above the surface and to have a 50% intensity point at 2 millimeters from the surface. In attempts to record spectra at higher pressures (50 and 100 psi), the continuum radiation increased to such an extent that the CN band was obscured, so that pressure effects could not be investigated. Povinelli also reported the results of some studies with a polyurethane binder, but he found that only faint OH and NH bands were present, whereas the PBAA binder had given OH, NH, CN, and CH. In no case did Povinelli or Selzer find any C_2 Swan bands.

Waesche (13) has carried out some preliminary investigation into the spectra of composite propellants burning at elevated pressures. Three different binder systems were investigated: PBAA, LP-3¹ (a polysulfide), and a polyurethane. It was found, in agreement with Povinelli's findings, that continuum radiation obscured meaningful emitters at pressures above 100 psi for the first propellant system. However, earlier work (14) had disclosed that the PBAA binder gave by far the "dirtiest" (sootiest) burning propellants. The LP-3 propellant, which was cleaner burning, could be examined up to 200 psi. The polyurethane, on the other hand, gives far less carbon radiation; spectra were obtained at pressures as high as 700 psi. These findings indicate that the pressure range over which emitters can be characterized is a strong function of the binder, since all three propellants were at approximately the same stoichiometry. The way in which the binder

¹ Trademark of Thiokol Chemical Corp., Trenton, New Jersey.

pyrolyzes has a strong effect, because luminous carbon must be present to have continuum radiation (unless some other solid reaction product can be formed, e. g., a metal oxide). In any case, these preliminary findings gave, for the first time, some promise that the behavior of the gas region as a function of pressure could be studied, i. e., how the emitters vary with pressure, both in relative concentration and in spatial distribution.

EXPERIMENTAL APPARATUS

The experimental set-up employs an adaptation of a micro window bomb (15) together with a grating spectrograph (Figs. 1 and 2). The propellant sample, $\frac{1}{4}$ inch wide, $\frac{1}{16}$ inch thick, and approximately $\frac{5}{8}$ inch long, is mounted in a sample holder (Fig. 3) which, in turn, is placed in the micro window bomb (Fig. 4). To allow transmission of ultra-violet radiation, the usual 2-inch-diameter tempered-glass windows of the bomb have been replaced by sapphire windows, 1 inch in diameter and $\frac{1}{8}$ inch thick. The windows are mounted in the bomb with the help of an adapter assembly (Fig. 5). Only part of the interior of the bomb need be viewable, since radiation from only a small portion of the window can be focussed on the spectrograph slit at any one time. In addition, the load-bearing area of the sapphire window is decreased, allowing the use of a thinner window and avoiding the distortions which can result from an overly thick component in the optical system. These sapphire windows have a high modulus of rupture (75,000 psi)-and have the additional advantage of not being subject to attack from the combustion-products of fluorine-containing propellants.

The image of the propellant sample is focussed on the spectrograph slit by a 50-millimeter-diameter quartz lens with a focal length of 150 millimeters. The magnification is approximately 0.8. Since the sample burning surface is perpendicular to the slit, the vertical position of an emitter on the film gives an indication of the emitter relative to the surface. The accuracy of location will be affected by the smearing coming from the cone of light accepted by the lens and from refractive effects. In addition, there will be an integrating effect resulting from the movement of the burning surface owing to propellant regression during exposure, so that exposure times should be as short as practicable. The exposure time is, of course, interrelated

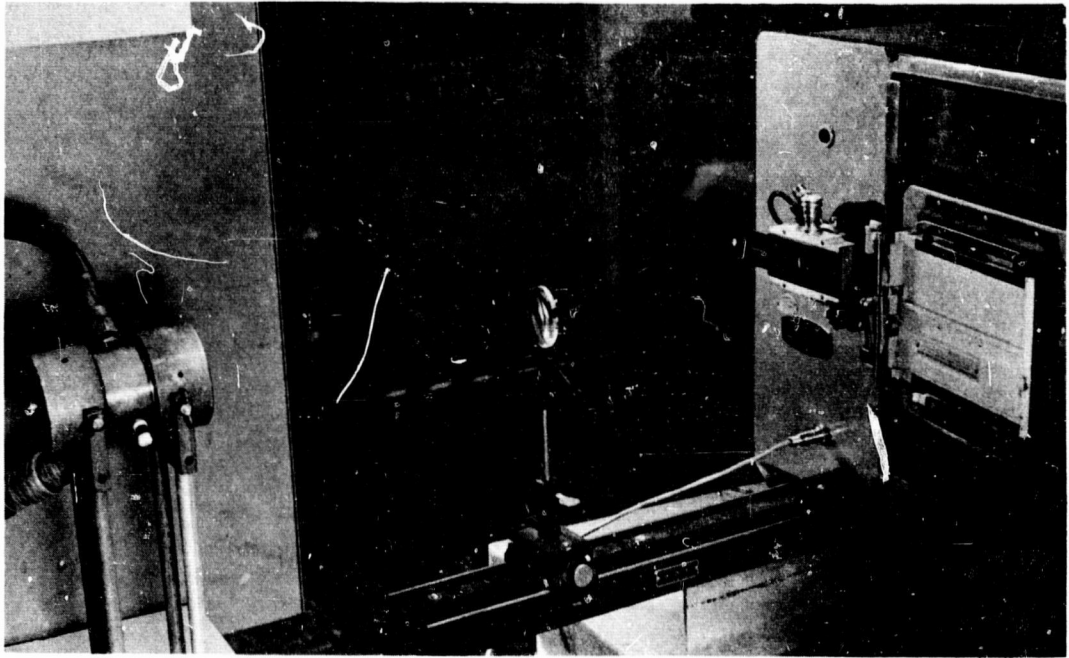


Fig. 1 Experimental arrangement for obtaining emission spectra of deflagrating solid propellants.

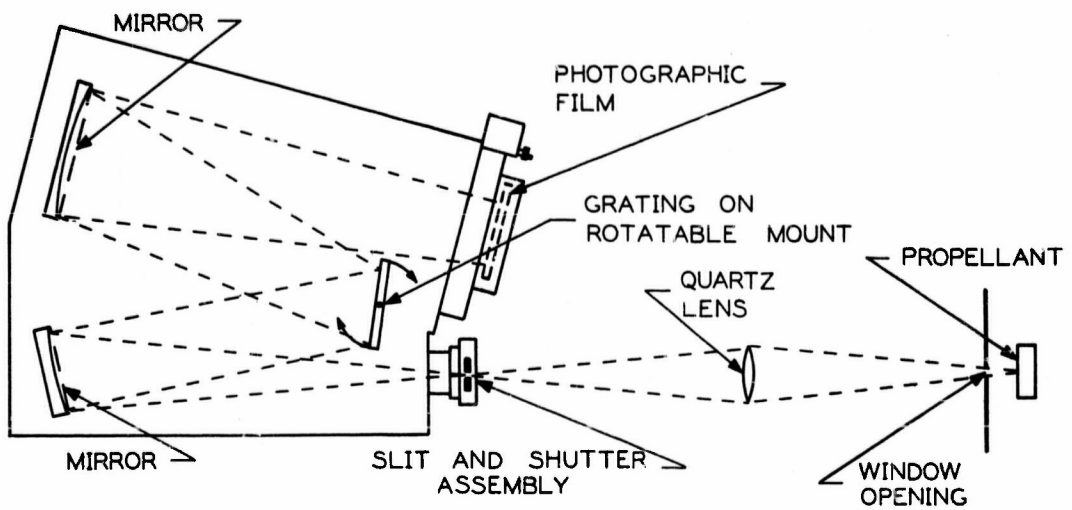


Fig. 2 Optics of experiment.

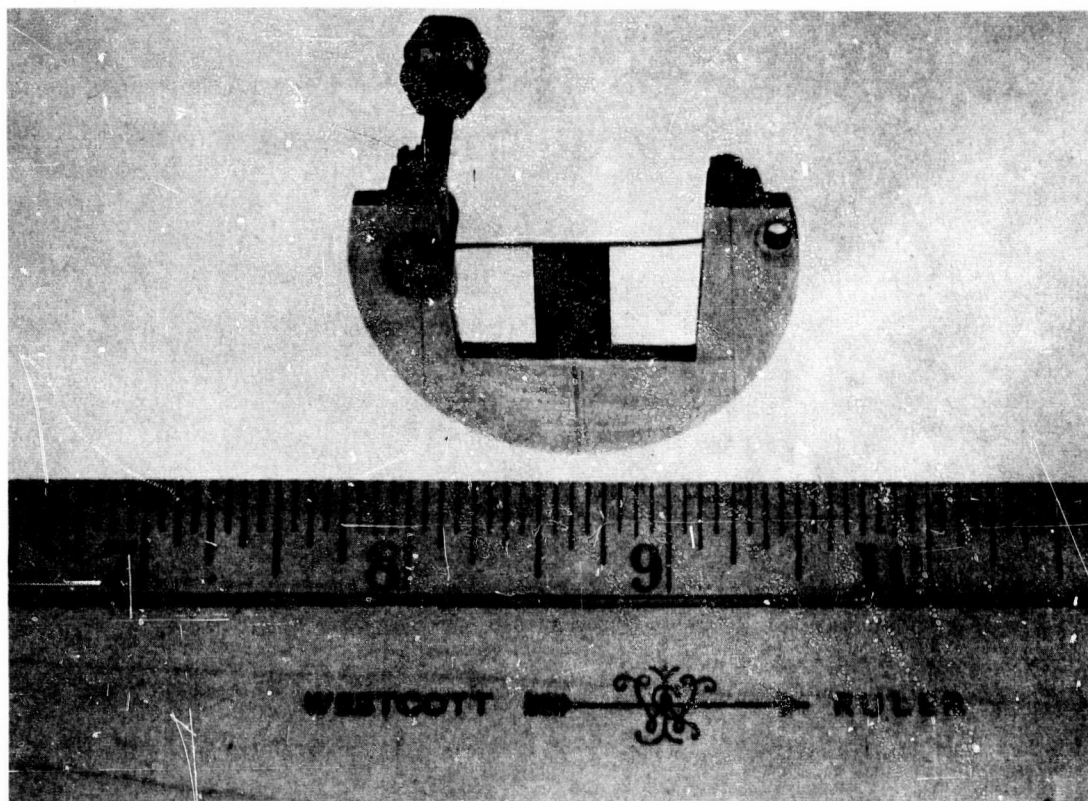


Fig. 3 Sample holder for micro window bomb.

with the cone angle of the lens system, which should be of the order of $f/4.5$ for best illumination efficiency, but which must have a higher f number if uncertainty resulting from the finite sample thickness is to be avoided. The sample thickness is another variable, since it affects the density of emitters in the line of sight, so that the interplay of these factors is a complex one.

The spectrograph is a Jarrell-Ash Model 75-000 $f/6.3$, 0.75-meter-focal-length, plane-grating spectrograph. A Czerny-Turner mount is used, with a 160-millimeter-diameter grating blazed at (nominally) 600 grooves/millimeter, giving a linear dispersion of approximately 20 Angstrom units/millimeter. The instrument, as received, had been modified to accept 4 × 5 inch Polaroid sheet film, but is also capable of accepting normal 5 × 7 inch photographic plates. It is possible to make an adapter to enable the use of 35 millimeter film, although only a 5-inch length would be used, corresponding to a range of 2500 \AA on a single exposure. The wavelength range for a particular exposure is determined by the angular

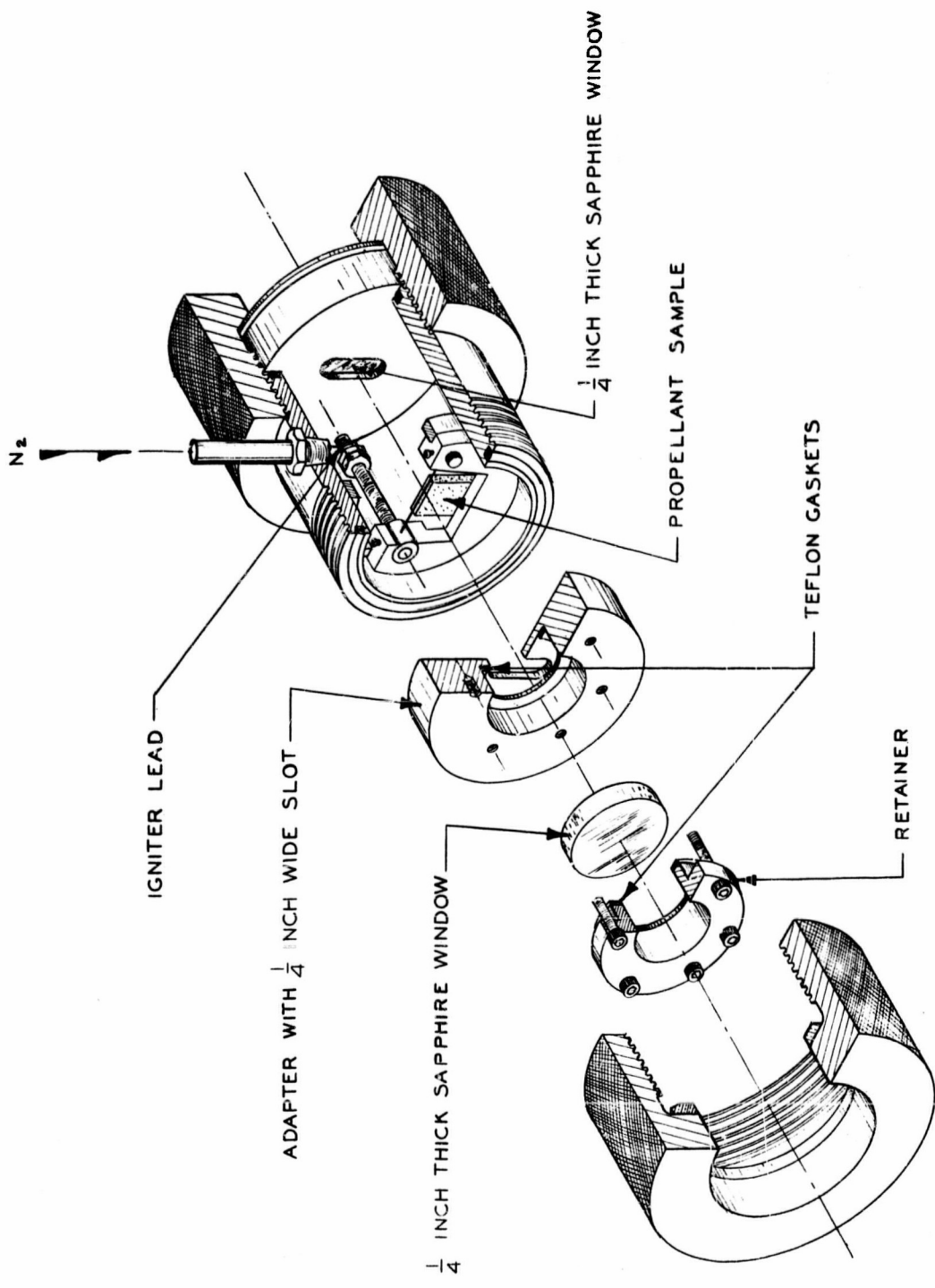


Fig. 4 Micro window bomb assembly.

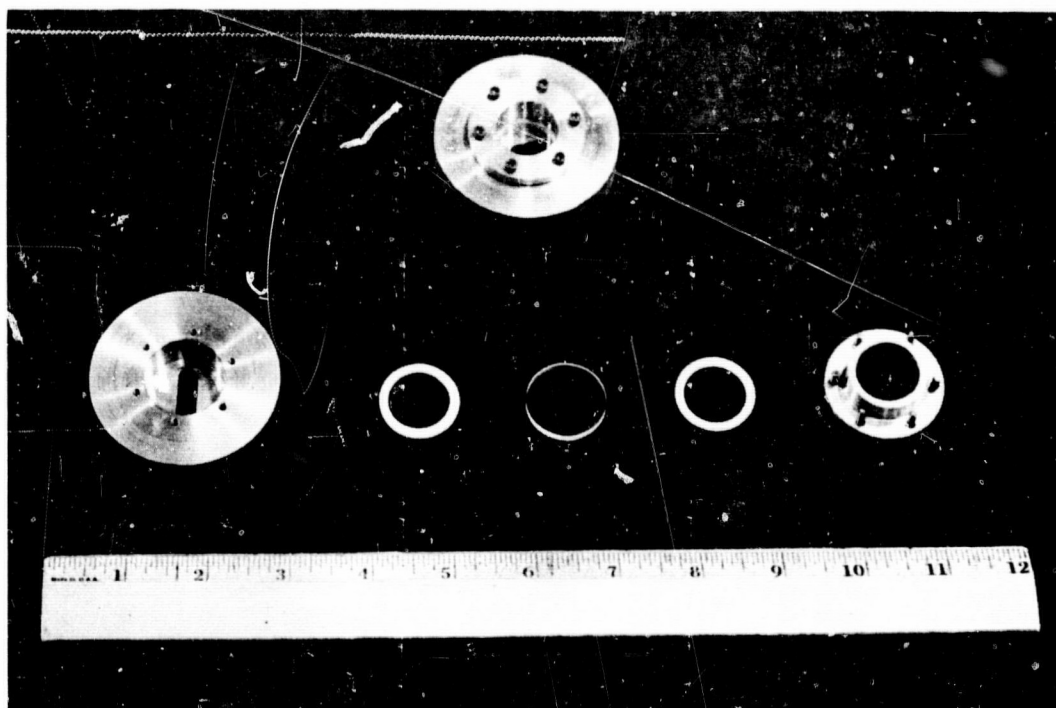


Fig. 5 Adapter used to mount sapphire window.

setting of the grating, which can be rotated by a gear train connected to an external knob. The instrument is capable of covering the spectral region from 2000 \AA to 10000 \AA , so that film sensitivity is limiting. (The $\frac{1}{8}$ -inch thick sapphire window has approximately 70% transmittance at 2000 \AA ; the quartz lens should transmit over 80% of light at this wavelength.)

The spectrograph slit width is adjustable up to 400 microns. For most tests, a width of 100μ has been used. In addition, a shutter is mounted behind the slit, with a range from $\frac{1}{400}$ second to 1 second, plus provision for time exposure. Depending on the particular test, exposure times from $\frac{1}{200}$ second to 1 second have been used.

The film most often used has been Polaroid Type 57 film, which has an ASA equivalent rating of 3000. Some tests have been run with Type 55 P/N film, with an ASA rating of 50. The spectral range of the Type 57 film was determined with the aid of a Black Light, Eastern Corporation Model SCT-1 mercury-vapor lamp, and was found to extend from about 2400 \AA to about 6500 \AA . The most sensitive range is from 3000 \AA to 5000 \AA . The mercury-vapor lamp is used after every test to provide a reference spectrum.

EXPERIMENTAL PROCEDURE

Ignition is accomplished with a hot-wire igniter pressed against the top of the strand (Fig. 2). 20-mil tungsten wire had been used to ignite samples for cinematographic studies of combustion (15); however, this type of wire remains intact, thereby introducing a source of continuum radiation, as well as giving unknown chemical effects. As a result, smaller-diameter nichrome V wire was substituted. After a series of trials, 28-gage (12-mil) wire was selected. The voltage used was also varied, since it was desired to have the wire break away, but only after the propellant had been ignited. Too low a voltage caused lengthy ignition delays, while too high a voltage led to wire breakage before ignition was accomplished. A voltage of about 12 volts was finally used.

Triggering of the spectrograph shutter was first accomplished manually. For the sake of reproducibility, automatic control was achieved by the use of a delay unit, which operated the shutter at a preset interval after the igniter voltage had been applied. The interval was adjusted such that steady-state burning was occurring and, in addition, such that no combustion products were filling up the bomb and obstructing the field of view. The smoke problem is most serious for high-burning-rate propellants, and some venting or surge-tank system may have to be used. At present, delays between $\frac{1}{5}$ and $\frac{1}{3}$ second are used. A Fairchild HS-101 motion analysis camera was used to take movies of ignition at 3000 frames per second. These movies, with a spark as a reference time, indicate that, for most conditions, ignition is completed and no smoke obscuration is evident when the shutter is triggered. Obscuration by combustion products is, of course, still a potential problem which becomes more serious for longer exposure times.

For those pictures where emitters were visible above the background, the emitters were identified as follows. The plate was first calibrated using the known lines of the mercury-vapor lamp. The positions were located by a Gaertner Serial No. 322 Coordinate Comparator, which was graduated in 0.01-millimeter divisions. The linear dispersion was then calculated. It was found that the dispersion increased from 19.6 \AA to 20.6 \AA /millimeter,

with decreasing wavelength, when the grating table was set to have 3600 Å in the middle of the spectrum, and increased from 18.9 Å to 20.0 Å/millimeter when 5200 Å was the center point. The positions of the flame emitters were then located relative to the closest mercury line, and the wavelength difference calculated. In this way, the wavelength of each emitter could be determined with some accuracy, limited mainly by the accuracy with which a band head or a line could be located. It was noted, from known lines, that the calculated reading was always about 5 Å high. This consistent error probably results from a slight malalignment of the plate holder, since the reference lines are put on after the plate has been moved by a rack-and-pinion gear. So far, the plate has always been moved in the same direction. Experiments will be run with the plate moved upward after a firing, rather than downward, as has been the case. In addition, when the reference line is put on by a fixed backlight, movement of the plate will no longer be necessary, as it is now, because of present difficulty in obtaining a uniform exposure with the small lamp.

Once the wavelength of an emitter has been determined, identification is made with the help of the compendium of molecular spectra by Pearse and Gaydon (16); atomic lines can be found in any convenient reference book. To aid in positive identification of a molecular emitter, the intensity of each band is noted and compared with the listed intensities. In this manner, overlapping bands can be sorted and identified.

EXPERIMENTAL RESULTS

Five different avenues of investigation were chosen. Initial feasibility studies are being made into each one, and the most promising ones will be investigated further. The different areas are as follows: (a) effect of various inert binders with ammonium perchlorate to see, for instance, how the polymeric material breaks down; (b) effect of various energetic binders with ammonium perchlorate, including the plastisol-nitrocellulose composite propellant type and the NF-propellant system; (c) effect of different oxygen/hydrogen, carbon/hydrogen, carbon/fluorine, and oxygen/fluorine ratios; (d) effect of aluminum as a function of pressure

and aluminum concentration and type to infer, from the presence or absence of the spectra of aluminum or its oxides, efficiency of combustion without motor firings; (e) effect of pressure and oxidizer particle size on flame-zone structure. This last area involves many of the first four, but with an added degree of complexity. Not only must the emitter be identified, but its spatial distribution in the gaseous flame must be determined. As mentioned previously, the accurate location of an emitter's position can be made only through the balancing of a number of optical factors.

Thus far, spectra have been obtained from four different propellants; an ammonium perchlorate-H-C (carboxy terminated polybutadiene) propellant, a plastisol-nitrocellulose composite propellant, and two NF propellants (Table I).

The H-C propellant, was burned at pressures from 10 psig to 250 psig, while the plastisol-nitrocellulose type was burned from 10 psig to 900 psig. Thus far, the NF propellants have been burned mainly at 10 psig because of their high burning rate and resulting smoke obscuration. Combustion-zone emitters are still identifiable at 200 psi with the NF propellants, and at 300 psi with the plastisol-nitrocellulose propellant. In the case of the H-C propellant, the continuum becomes a serious problem at lower pressures.

The following comparisons can be made among the three types of propellant for some different flame emitters:

- (1) OH bands (heads at $3064 \overset{\circ}{\text{A}}$ and $2811 \overset{\circ}{\text{A}}$) are strong in every case - stronger, in fact, than those found by Sutherland and Selzer for samples burning in air.
- (2) NH band ($3370 \overset{\circ}{\text{A}}$) is strongest in the H-C propellant and weakest in the plastisol-nitrocellulose composite propellant.
- (3) CH bands ($4215 \overset{\circ}{\text{A}}$ and $3900 \overset{\circ}{\text{A}}$) are present in the flames of the H-C and the NF propellants, but not in the plastisol-nitrocellulose propellant.
- (4) CN violet bands ($4216 \overset{\circ}{\text{A}}$, $3883 \overset{\circ}{\text{A}}$, and $3590 \overset{\circ}{\text{A}}$) are stronger with the NF formulations, and weaker in the nitrocellulose ones.

Other emitters are also present. Among these are the spectra characteristic of impurities - Na, Ca, CaCl, CaOH, K, Cu - and the bands of excited N₂. In addition, some HF emission is present from the NF propellant, although the film sensitivity is such that the emitters fall outside the range of highest

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Table I
Propellant Formulations

	RH-C-39 (Batch 100)	RH-P-120 (Batch 3)	RH-SA-160 A (Bk. 306-85)	RH-SA-179 (Bk. 306-104)
Ammonium Perchlorate, 56 μ	59.50	47.6	60.0	60.0
Ammonium Perchlorate, 8 μ	25.50	-	-	-
ZL-434 ^a	9.42	-	-	-
ERLA-0510 ^b	0.13	-	-	-
MAPO ^c	0.35	-	-	-
Iron Linoleate	0.10	-	-	-
Diethyl Adipate	5.00	-	-	-
Double-base powder ^d	-	15.9	-	-
TEGDN plasticizer ^e	-	36.5	-	-
NFPA monomer ^f	-	-	20.0	20.0
APA plasticizer ^g	-	-	20.0	-
TVOPA plasticizer ^h	-	-	-	20.0
X-970 crosslinker ⁱ	-	-	0.2 added	0.2 added
GDB initiator ^j	-	-	0.1 added	0.1 added

^a Carboxy-terminated polybutadiene polymer (Thiokol Chemical Corp.)

^b Trifunctional epoxide (Bakelite Division, Union Carbide)

^c Tris[1-(2-methyl)aziridinyl]phosphine oxide (Interchemical Corp.)

^d Ball Powder containing no carbon black

^e Triethylene glycol dinitrate

^f 2,3-Bis(difluoramino)propyl acrylate

^g 2,3-Bis(difluoramino)propyl propionate

^h 1,2,3-Tris(α , β -bis[difluoramino]ethoxy)propane

ⁱ 1,3-Butanediyl dimethacrylate

^j Bis(chlorobenzoyl)peroxide

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response, since the electronically excited states emit at 2670 \AA and below (17), while the vibration-rotation bands are mainly in the infrared (18). The NO γ -bands also appear, but only at low pressures, and are not strong. Other bands are present, and may be tentatively ascribed to CHO, the presence of which Selzer also suspected (11), but was never able to substantiate.

As for the spatial distribution of emitters little can be said at this initial stage. With the NF propellants, the luminosity is such that exposure times as short as $\frac{1}{100}$ second can be used, so that the burning surface regresses very little during exposure. The CN bands extend vertically about 3 millimeters, indicating that some reaction is occurring over this spatial extent, at least at the pressure used (10 psig). Further tests will be made at higher pressure with shorter exposures.

Additional tests were made to see to what extent components of the optical system could introduce uncertainty into the spatial location of an emitter. This was done by taping over a portion of either the spectrograph slit or the bomb and observing the sharpness with which illumination was cut off. It was found that, in every case, those emitters characteristic only of combustion were not visible when radiation from only the top portion of the window was allowed to reach the film. This does not preclude the possibility that the spectrograph's internal optics contribute a degree of uncertainty, but the clear demarcation lines observed on the spectra, corresponding to the tape location, argue against this possibility.

CONCLUSIONS AND FUTURE PLANS

Although the above results are only preliminary, some conclusion about future plans can be drawn from them. It appears that the feasibility of the spectrographic technique has been demonstrated, although the useful pressure range will be limited, for a number of propellants, by the presence of luminous carbon. The use of thicker strands will help in the intensification of emitters, as well as cutting down on any possible edge effects.

Work will continue with the NF propellants at higher pressures, using shorter exposure times. Film of different sensitivity will be investigated

to enable closer study of the HF emission, which should be a key factor in determining the efficiency of this class of propellant. Ordinary negative film will also permit quantitative mapping of the emitters, not possible from Polaroid positives.

The optical system will also be revised slightly. A lens with a longer focal length can be used and a backlighting arrangement can be added. The former will give a smaller cone angle and will reduce distortion, while the latter will eliminate the need for moving the film to obtain a reference and will enable shadow techniques to be used to locate the surface.

The detailed efforts into the different research areas outlined will, of course, depend on the initial results obtained. In any case, the spectrographic observation of combustion emitters should be able to add fundamental knowledge to the field of solid propellant deflagration.

REFERENCES

1. Sutherland, G. S., "Mechanism of Combustion of an Ammonium Perchlorate-Polyester Resin Composite Solid Propellant," Ph.D. Dissertation, Princeton University, Dept. of Aeronautical Engrg., 1956
2. Penzias, G. J., Liang, E. T., and Tourin, R. H., "Infrared Radiation and Temperature Measurements in Solid Propellant Flames I. Preliminary Study of Arcite 368," Warner and Swasey Company, TR-800-5, Oct. 1962.
3. Povinelli, L. A., "Study of Composite Solid-Propellant Flame Structure Using a Spectral Radiation Shadowgraph Technique," Lewis Research Center NASA TM X-52071, 1964.
4. Sabadell, A. J., "The Measurement of the Temperature Profiles of Burning Solid Propellants by Microthermocouples," Princeton University, Dept. of Aeronautical Engrg., September 1963.
5. See, for instance: (a) Gaydon, A. G., "The Spectroscopy of Flames," John Wiley & Sons (New York), 1957. (b) Gaydon, A. G., "Spectroscopy and Combustion Theory," Chapman and Hall Ltd. (London), 1948. (c) Gaydon, A. G., and Wolfhard, H. G., "Flames," Macmillan Company (New York), 1960.
6. Mavrodineanu, R., and Boiteux, H., "Flame Spectroscopy," John Wiley & Sons (New York), 1965.
7. Sotter, J. G., "Chemistry and Combustion Instability in Solid Propellant Rocket Motors," Ph.D. Dissertation, University of Sheffield (U. K.), Dept. of Fuel Tech. and Chem. Engrg., Oct. 1964.
8. Heath, G. A., and Hirst, R., "Some Characteristics of the High Pressure Combustion of Double-Base Propellant," 8th Symposium (International) on Combustion, Williams & Wilkins (Baltimore), 1962, pp. 711-720.
9. Rekers, R. G., and Villars, D. S., "Flame Zone Spectroscopy of Solid Propellants. II," J. Opt. Soc. Amer. 46, 534-537 (1956).
10. Rössler, F., "Optische Untersuchungen bei der adiabatischen Verbrennung von festen Treibmitteln," Z. Angew. Phys. 6, 175-182 (1954).
11. Selzer, H., "Über den Verbrennungsmechanismus von Composite-Treibstoffen," Raketentech, Ramfahrtforsch. 2, 41-46 (1963).

12. Selzer, H., private communication, December 1964.
13. Waesche, R. H. W., Princeton University, unpublished work 1964.
14. Hall, K. P., Wenograd, J., Cole, R. B., and Summerfield, M., "Burning Rate Control Factors in Solid Propellants," Princeton University Aeronautical Engineering Report No. 446-m, July 1962.
15. Thompson, B. L., Rohm & Haas Company, Quarterly Progress Report on Interior Ballistics, No. P-64-22, November 1964.
16. Pearse, R. W. B., and Gaydon, A. G., "The Identification of Molecular Spectra," John Wiley & Sons (New York), 1950.
17. Johns, J. W. C., and Barrow, R. F., "The Ultra-Violet Spectra of HF and DF," Proc. Roy. Soc. A 251, 504-518 (1959).
18. Mann, D. E., Thrush, B. A., Lide, D. R., Ball, J. J., and Acquista, N., "Spectroscopy of Fluorine Flames. I. Hydrogen-Fluorine Flame and the Vibration-Rotation Emission Spectrum of HF," J. Chem. Phys. 34, (1961) 420-431.

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