An Infrared Microspectroscopy Method for Determining Deterrent Penetration in Nitrocellulose-Based Propellant Grains

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Synopsis

Infrared microscopy was used to determine di-*n*-butyl phthalate, dinitrotoluene, and methyl centralite diffusion profiles in cross sections of nitrocellulose-based propellant grains. Absorbance of marker functional groups was determined at 25–50 μm intervals from the edge to the center of the sections. Comparison of IR and light microscopical data indicated that the optically visible boundary does not define the entire depth of deterrent penetration into propellant grains.

INTRODUCTION

Deterrents are materials that are applied to small arms nitrocellulose-based propellant grains to control the initial burning rate, and thus avoid overpressure early in the ballistic cycle. Ballistic performance is thought to be related to the depth of deterrent penetration into the smokeless powder grains. Reliable methods for determining deterrent penetration profiles are, therefore, necessary for predicting performance.

Light microscopical methods in conjunction with staining or autoradiography have been used to study the depth of deterrent penetration with nitrocellulose propellant grains.[1-8] Except for the autoradiography method,[4] staining methods provide only an indirect measure of deterrent penetration. Although autoradiographic methods are useful, they are ridden with manipulative problems. Sections must be completely flat and in intimate contact with the photographic film during exposure or discontinuities in the autoradiograms are observed. Furthermore, self-adsorption of β-particles results in difficulties in defining the inner boundary of deterrent penetration. Resistance to diffusional flow across the interface between unlabelled and labelled matrix regions is also a source of potential error in radiolabelling experiments.[9] Recent developments in Fourier-transform infrared (FTIR) microspectroscopy have made it possible to determine chemical functional groups rapidly in samples as small as 10 μm in diameter. This report describes a direct method for determining deterrent penetration in smokeless powders using microtomy and IR microscopy. Comparisons with light microscopical data are also presented.

EXPERIMENTAL

Propellants. Deterred propellants manufactured by DuPont (IMR 4350, lot 6402), Olin (WC870, lot 291), and Expro (30 mm) were studied. The deterrents used on the propellants were dinitrotoluene (DNT), di-*n*-butyl
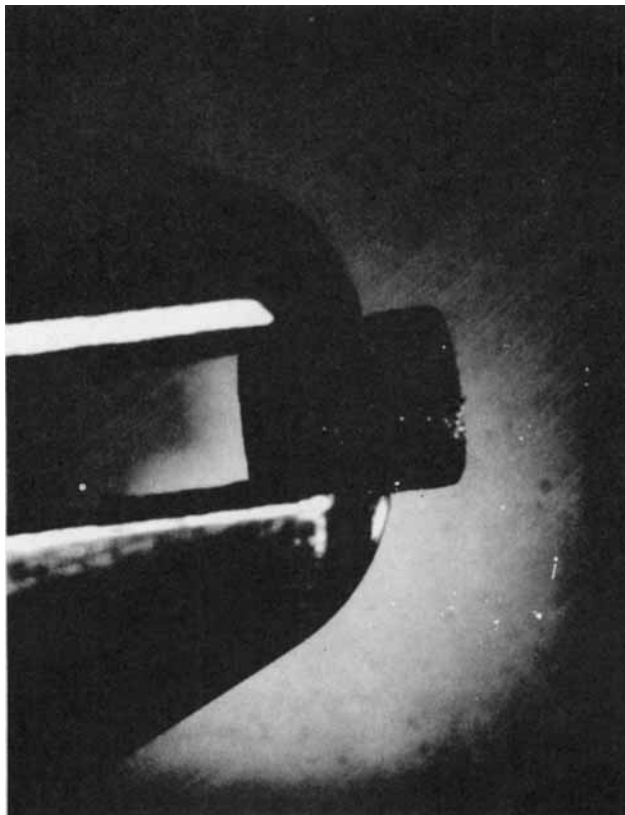
Fig. 1. Propellant grain clamped in an LKB microtome chuck in preparation for thin sectioning.

phthalate (DBP), and methyl centralite (N, N'-dimethyl–N, N'-diphenyl-urea), respectively. The DuPont and Expro samples are extruded powders; the Olin sample is a ball powder.

Microtomy. Our preliminary work indicated that we would need sections > 10 μm thick. Since it is extremely difficult to obtain uniform sections below 10 μm using a sledge microtome and stainless steel blade, an LKB ultramicrotome (Gaithersburg, MD) and glass knives were used. Using this precision instrument, section thickness can be controlled within $\pm 10\%$ of the desired value. Propellants were clamped directly into LKB microtome chucks (Fig. 1) without embedding in glue or epoxy resin. Grains were microtomed until a center cross section was obtained. Sections 3-μm thick were then collected from the center of the grain for analysis.

Infrared Microspectroscopy. An Analect AQM-515 infrared microscope (Utica, NY) module mounted on an Analect AQS-20M Fourier-transform spectrometer was used in this study. A narrow band MCT (HgCdTe) detector in the microscope module gives high sensitivity in the 4000–700 cm^{-1} range. Propellant cross sections were placed on 6-mm diameter KCl crystals and infrared spectra were taken at 25–50 μm intervals from the outer edge to the center of the section by manually positioning the circular IR variable beam
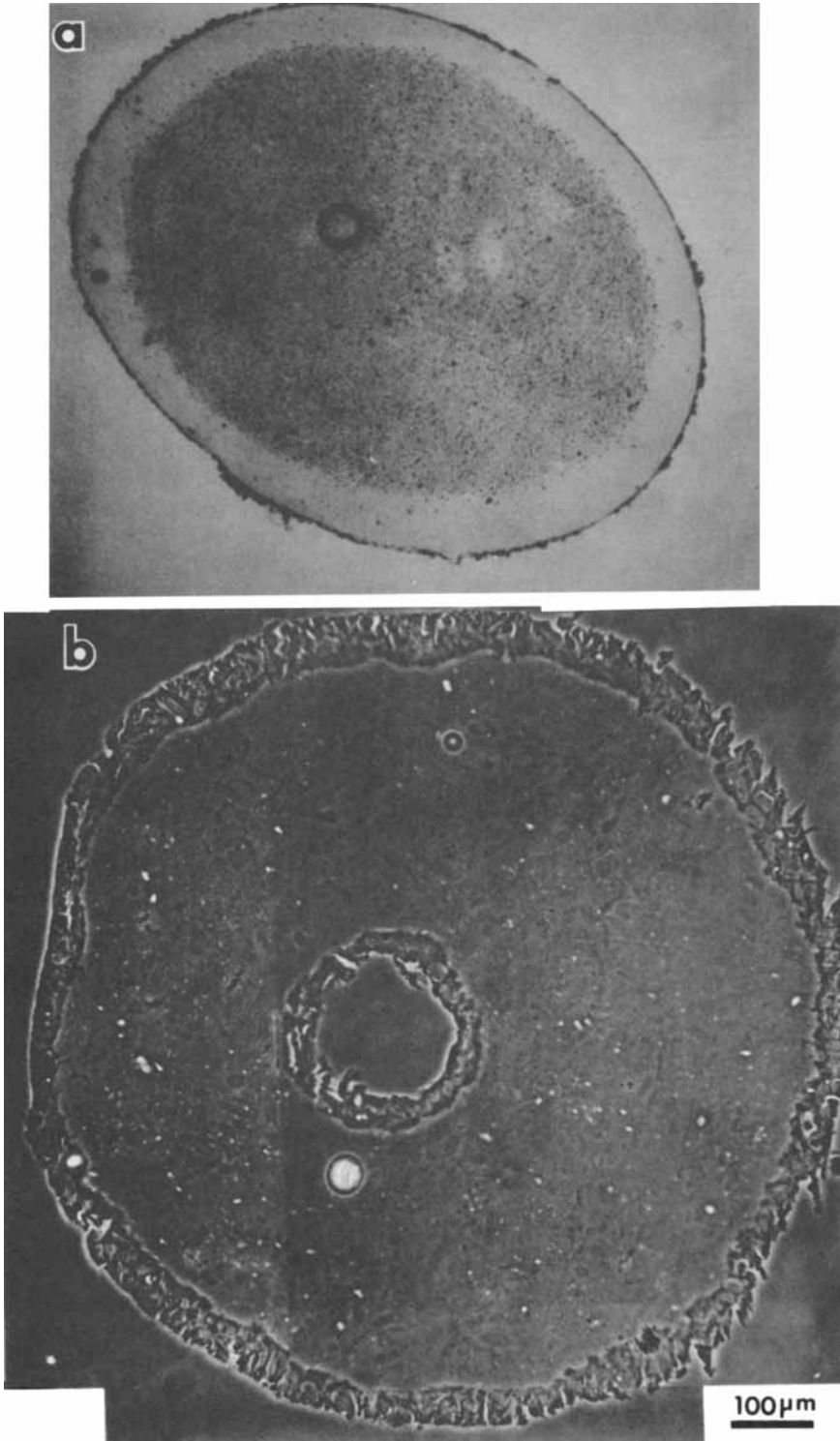
Fig. 2. Cross section of deterred propellant grains: (a) brightfield image of a DBP-deterred grain, and (b) phase contrast image of DNT-deterred grain.

stop aperture along the section using the horizontal and vertical stage controls. Infrared and visible light paths are coincident so that the area that is visually selected is the area that is analyzed. The size of the analysis area was chosen based on the cross-sectional diameter of the propellant grains. Infrared measurements were taken at 25-μm intervals for the Olin and DuPont propellants and at 50-μm intervals for Expro. The beam stop aperature was calibrated with a standard micro-calibration slide (Carl Zeiss, Germany). Infrared measurements were taken across the grain until zero absorbance of the marker band was detected; this was defined as the inner boundary of the deterrent layer. In calculating absorbance, the background was automatically subtracted using a software program. The IR was operated at a resolution of 4 cm^{-1}; 100 scans of each 25–50 μm area were acquired. The standard deviation for replicate absorbance readings at the same spacial location on different thin sections of the same grain was 6%.

Light Microscopy. After the IR analysis of each cross section, the same sections were mounted in mineral oil and viewed using brightfield or phase contrast optics (Olympus BH-2) at 120 ×. Brightfield microscopy can be used to study the optically visible deterrent layer in propellants only if the refractive index of the deterred layer is 1/4 λ different from the undeterred portion of the grain so that enough contrast is generated. DBP effectively changes the refractive index of the nitrocellulose (NC) matrix so this deterrent can be readily visualized using brightfield microscopy [Fig 2(a)]. Because DNT and methyl centralite do not appropriately alter the refractive index of the NC matrix, a phase plate (and phase contrast microscopy) was used to accentuate those differences [Fig. 2(b)]. Polarization microscopy was not useful in determining the deterrent layer in these samples since no birefringent layer was observed. In determining the "apparent" deterrent penetration depth from light micrographs, three measurements were taken from each section derived from four propellant grains. The mean and standard deviation were calculated. Diameters of the grains were determined from measurements of photographic images taken at 120 ×. All photomicrographs were taken using Polaroid type 57 positive film.

RESULTS AND DISCUSSION

Method Requirements

The principal requirement in the development of an IR microspectroscopy method for monitoring deterrent penetration into smokeless powders is that the diffusant absorb strongly at a frequency where there is relatively little absorption by the matrix. For example, infrared spectra of thin sections of DBP-coated grains reveal a carbonyl absorption band at 1717 cm^{-1} in spectra of the coated grains [Fig. 3(b)], which is not present in spectra of the uncoated nitrocellulose propellant [Fig. 3(a)]. This band can be used as a marker for determining the DBP-deterrent gradient across the grains. The R–NO$_2$ band at 1534 cm^{-1} [Fig. 4(a)] was used to monitor the DNT deterrent in the DuPont samples, and the marker band for methyl centralite-coated propellants was the C—C ring stretching band [Fig. 4(b)] at 1594 cm^{-1}.
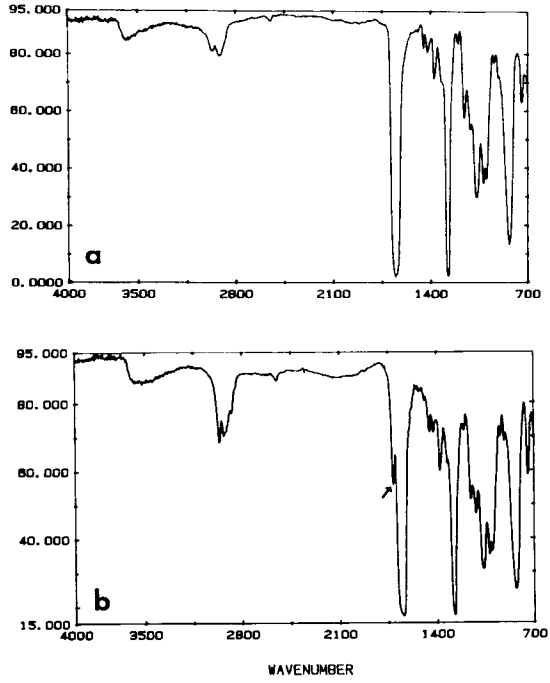
Fig. 3. Infrared spectra of thin sections of uncoated nitrocellulose-based propellant (a) and DPB-coated propellant (b). Y axis = %T.
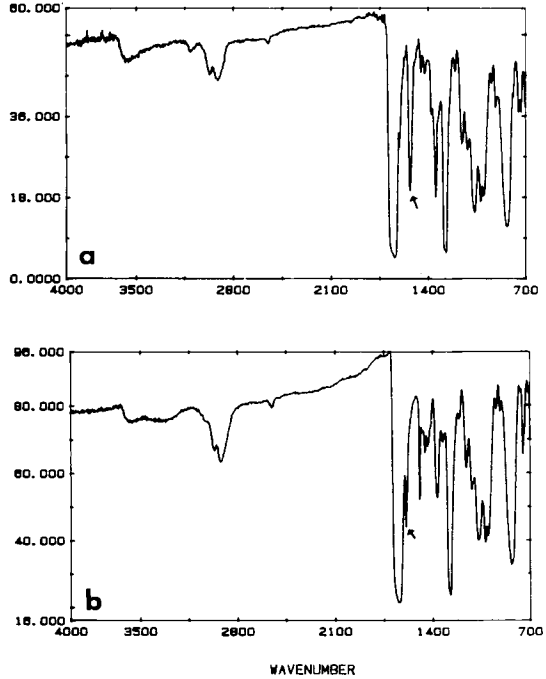

Fig. 4. Infrared spectra of thin-sections of DNT-coated propellant (a) and methyl-centralite-coated propellant (b). Y axis = %T.
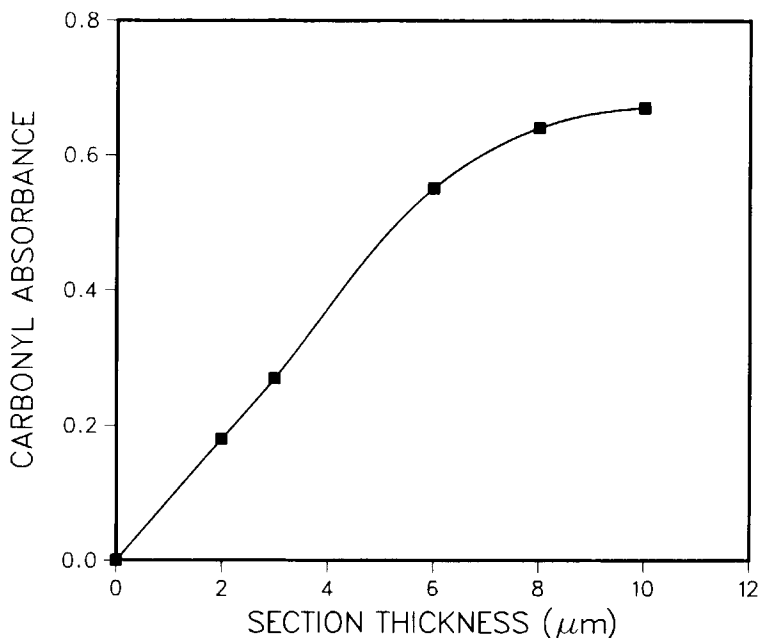
Fig. 5. Infrared absorbance as a function of section thickness for the DBP marker band at 1717 cm^{-1}.

An equally important requirement of the IR method is that uniformly thick cross sections be produced for the analysis. Absorbance values for the marker band depend on section thickness as well as deterrent concentration at any point in the cross-section. The effect of section thickness on absorbance for the 1717 cm^{-1} band for DBP-deterred grains is shown in Figure 5. The relationship between section thickness and absorbance is seen to be linear up to 6 μm. Above this value the data show a sharp deviation from linearity.

It is often a common practice to embed propellant grains in an epoxy or glue to stabilize them for thin sectioning.[4,5] Embedding the propellant grains in Titebond (Franklin Glue Co.). did not interfere with the IR determination of deterrent penetration. No absorption bands for the glue were observed in sections of propellant grains.

Based on our preliminary studies as well as manipulative considerations, our method of choice was to use 3-μm thin sections from unembedded propellant grains. During sectioning, a needle was used as an antiroll guide to prevent sections from curling.

Deterrent Penetration in Propellant Grains

The deterrent profiles for the three commercial samples are shown in Figures 6–8. Each curve in the figures represents the data obtained from one propellant grain. Four grains from each sample were analyzed. About half of the grains that were examined showed a deterrent concentration profile resembling the sharp step function described by Brodman et al.[4] i.e., a level deterrent concentration through a region of the grain followed by a sudden
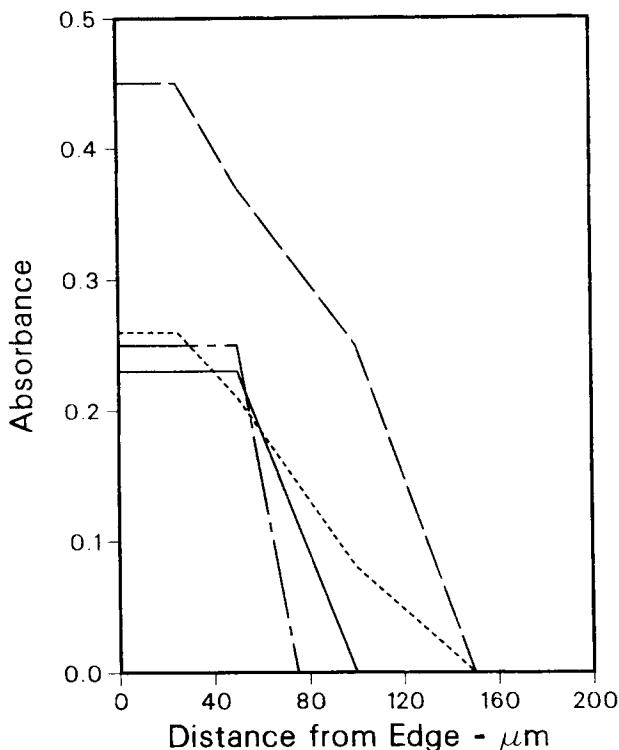
Fig. 6.   Cross-sectional deterrent concentration profiles of four different DBP-coated Olin WC870 propellant grains as determined by infrared absorbance at 1717 cm^{-1}.

drop in concentration. The other half of the propellants showed a more gradual decrease in deterrent concentration following an initial high concentration at the edge. This was particularly true for two of the methyl centralite-coated grains (Fig. 8).

The IR spectra taken in the deterred regions of DBP-coated propellants showed a shift in the ν(OH) frequency to 3516 from 3568 cm^{-1} in the undeterred grain (Table I). A shift in the DBP ν(C=O) frequency to 1717 cm^{-1} in the nitrocellulose-based propellant [Fig. 3(b)] compared with 1737 cm^{-1} in the spectrum of the deterrent alone was also observed. These data suggest that H-bonding occurred between the deterrent carbonyl and unesterified hydroxyls on nitrocellulose, which is in agreement with the model studies by Brodman et al.[10] Brodman's[5] hypothesis that a sharp DBP diffusion profile in nitrocellulose-based propellant grains is caused by a diffusion with interaction mechanism appears to be substantiated by our data.

A study of free ν(OH) frequencies in deterred and nondeterred regions of cross sections of DNT- and methyl-centralite-deterred grains also provided evidence for hydrogen bonding between deterrent and nitrocellulose matrix (Table I). Again these data agree with a diffusion with interaction mechanism for deterrent penetration in nitrocellulose-based propellant grains.

The deterrent profiles in Figures 6–8 indicate that deterrent concentration and depth of penetration varied among the commercial samples. The Expro methyl centralite deterrent showed deeper penetration into the propellant
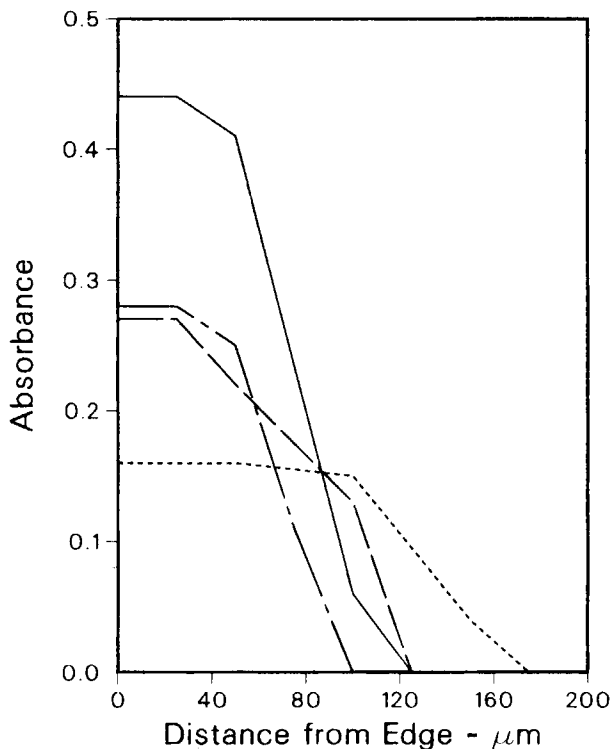
Fig. 7. Cross-sectional deterrent concentration profiles of four different DNT-coated DuPont IMR 4350 propellant grains as determined by infrared absorbance at 1534 cm^{-1}.

grains than what was observed for DNP- and DBP-deterred propellants. Variations in deterrent profiles among the three samples studied are related to different proprietary base formulations as well as different processing methods that affect the diffusion of deterrent into the propellant grains. The physical characteristics of the propellant matrix as well as the deterrent carrier solvent and deterrent structure, and concentration, are the major factors governing deterrent penetration depth. Fong and Cooke[7] have observed differences in deterrent penetration rates as a function of solvent polarity and deterrent chemical structure.

The deterrent profiles also varied greatly from grain to grain within the same sample. This was particularly evident in differences in absorbance level at the beginning of any profile. Many commercial methods of coating propellant grains are batch operations where the deterrent in a suitable solvent is added to a drum of aggetated grains. Such methods do not allow for uniform coating distribution throughout the batch so that variations in coating coverage among grains is not unexpected.

Measurement of the optically visible deterrent layer on light micrographs indicated that the penetration depth in the various propellants was 72 ± 10 μm for Olin WC 870, 58 ± 2 μm for DuPont IMR 4350, and 103 ± 15 μm for Expro. Deterrent measurements on Olin WC 870 are in good agreement with the light microscopical data of Brodman et al.[5] who observed a 64–73 μm DBP penetration depth at deterrent concentrations of 8.5–9.5%. Similarly,
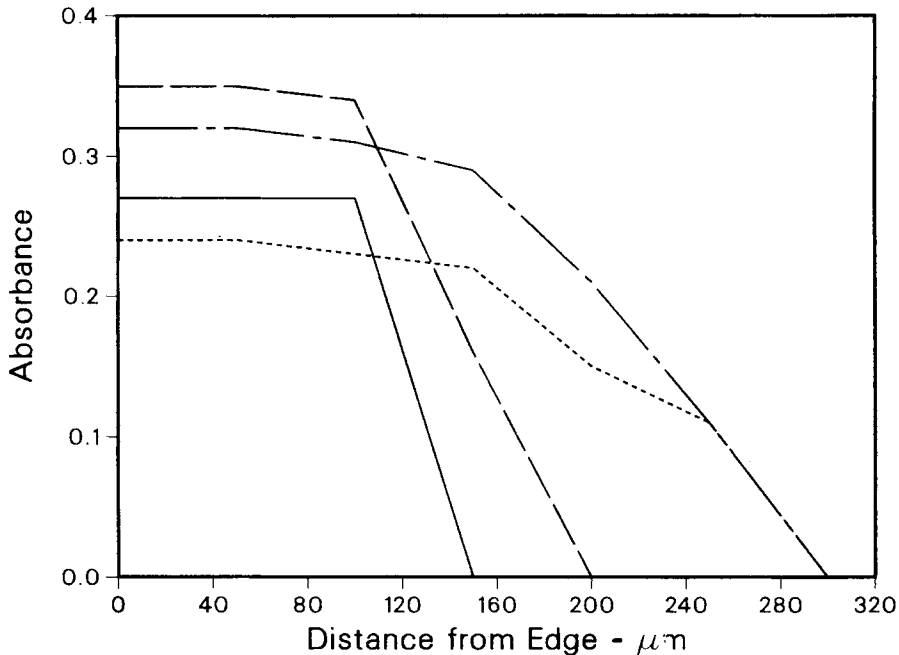
Fig. 8. Cross-sectional deterrent concentration profiles of four different methyl centralite-coated Expro grains as determined by infrared absorbance at 1594 cm^{-1}.

TABLE I

Free ν(OH) Frequencies (cm^{-1}) in Nondeterred and Deterred Regions in Cross Sections
of Deterred Nitrocellulose-Based Propellants

Propellant grain	Nondeterred region	Deterred
Olin (DBP)	3568	3516
DuPont (DNT)	3587	3579
Expro (CH$_3$–centralite)	3588	3548

Stiefel[11] observed an average deterrent penetration of 53 μm into DuPont IMR 4350 propellant grains which agrees with our light microscopical data.

Deterrent penetration measurements on light micrographs of propellants do not directly correspond to the depth of deterrent penetration as determined by IR microscopy. Two of the four Olin grains showed IR deterrent penetrations greater than 150 μm (Fig. 6). All of the DuPont propellants (Fig. 7) showed IR deterrent penetration greater than the measured 58 μm. Similarly, deterrent in three of the four Expro grains (Fig. 8) penetrated to a depth greater than the 103 μm determined microscopically.

CONCLUSIONS

Infrared microscopy clearly indicates that the depth of the deterrent layer observed by light microscopy is not the entire penetration depth. In most instances, the deterrent is detected well beyond the visible boundary. It is

likely that this visible boundary includes a high concentration of deterrent molecules that are bound tightly through hydrogen bonding between carbonyl or other polar groups of the deterrent and the unesterified hydroxyl groups in nitrocellulose, i.e., Brodman's[5] diffusion with interaction mechanisms. Once all of the nonesterified hydroxyls on the nitrocellulose have been saturated in these regions, the remaining deterrent molecules are free to diffuse deeper into the propellant matrix. Deterrent detected in areas beyond the microscopically visible boundary by infrared is possible because of the high sensitivity, i.e., low detection limit of the method.

The accuracy of the infrared microspectroscopy method for determining deterrent penetration into grains could be greatly improved by using a precision micrometer stage to dial in the exact area for IR analysis instead of relying on visual determination of size by a manual operator. Microtoming operations may be reduced if a micro-reflectance detector were used. Neither of these instrument capabilities were available at the time of this study.

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