

The Application of Infrared Microimaging for the Determination of the Distribution, Penetration Depth, and Diffusion Profile of Methyl Centralite and Dibutyl Phthalate Deterrents in Nitrocellulose Monoperforated Propellant

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SYNOPSIS

Infrared microspectroscopy was used to determine quantitatively and qualitatively methyl centralite (MC) and dibutyl phthalate (DBP) diffusion profiles in cross sections of nitrocellulose-based monoperforated propellant grains. The absorbance values of the C=O peak of DBP at 1717 cm^{-1} and the aromatic C—C peak of MC at 1496 cm^{-1} were measured relative to the NO₂ overtone peak of the nitrocellulose at 2555 cm^{-1} at 10 μm intervals from the outside edge inward (external profile) and the perforation edge inward (internal profile). Infrared microimaging was used to determine the distribution and penetration depth of the DBP and MC using the C=O peak of DBP at 1717 cm^{-1} and the aromatic C—C peak of MC at 1496 cm^{-1} as diagnostic of the two deterrents to obtain the contour and axonometric displays of the distribution. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Deterrents (moderants) are materials that are diffused into single-based nitrocellulose (NC) and double-based nitrocellulose/nitroglycerine (NC/NG) small-arms propellant grains to modify the initial burning rate at the surface of the propellant and, hence, the rate of gas evolution. This avoids overpressure early in the ballistic cycle. Ballistic performance is thought to be related to the concentration and depth of penetration of the deterrent into the propellant grains. Therefore, reliable analytical methods for the qualitative and quantitative determination of the concentration and depth penetration for the prediction of ballistic performance are required.

Established methods for measuring the penetration depth of moderants into NC propellant grains include various staining and optical techniques¹⁻⁴;

however, these techniques were not capable of directly measuring the concentration profile of moderants into the grains. Until recently, to measure the concentration profile of the moderant required the use of specially prepared deterred propellants containing ¹⁴C-radioisotope-labeled deterrents and autoradiographic^{5,6} and scintillation counting procedures.⁷ Autoradiographic methods are useful but they have manipulative problems: Sections must be completely flat and in intimate contact with the photographic film during exposure or discontinuities in the autoradiograms are observed. Also, self-absorption of B-particles results in difficulties in defining the inner boundary of deterrent penetration.

Recently, we reported a laser Raman microspectroscopic method⁸ for determining the penetration depth and qualitative and quantitative diffusion profiles for methyl centralite in NC and NC/NG matrices. An infrared⁹ microspectroscopic method has also been reported for determining the penetration depth and qualitative diffusion profiles of dinitrotoluene, dibutyl phthalate, and methyl centralite.

Infrared microimaging¹¹ is achieved by coupling

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a computer-controlled, two-dimensional motorized stage to an infrared microscope. A series of infrared spectra are then obtained at specified X and Y coordinates of the sample. A single image will represent the intensity of a specific frequency over the spatial range of the sample. Different images based on different functional groups can be obtained by choosing various frequencies to be displayed.

In this paper, we report on an infrared method for the quantitative measurement of dibutyl phthalate and methyl centralite diffused into the same matrix of NC and an infrared imaging method for the distribution of the deterrents. The methods can also be applied to other deterrent systems.

EXPERIMENTAL

Deterring Process

The required quantities of propellant base grain, methyl centralite, dibutyl phthalate, and water are added to a "Sweetie pan." Steam is injected directly into the rotating pan, allowing the temperature to rise to 90–95°C, and then it is held there for 30 min. After coating is completed, the contents of the pan are placed in a hessian bag and subjected to a hot water steep (90–95°C) for 22 h. The powders are then air-dried at 43°C.

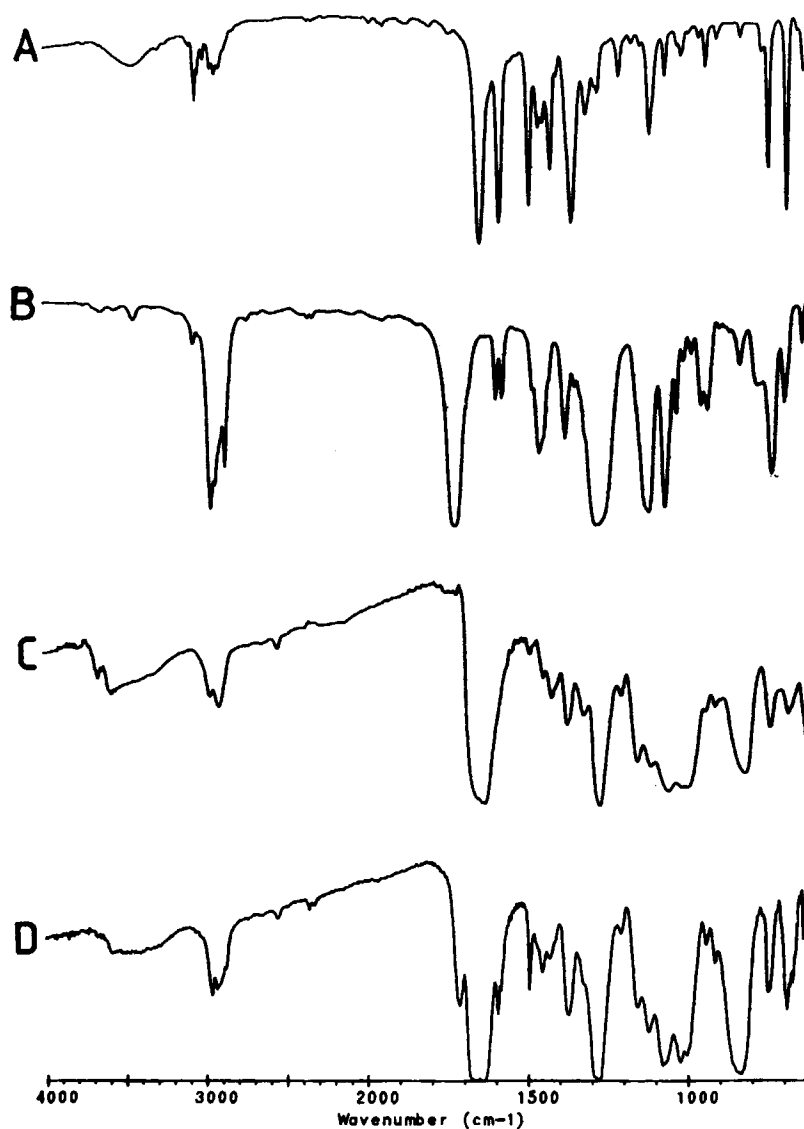


Figure 1 Reference IR spectra of (A) MC, (B) DBP, (C) NC base grain, and (D) MC/DBP deterred NC grain. Spectral range 4000–625 cm^{-1} .

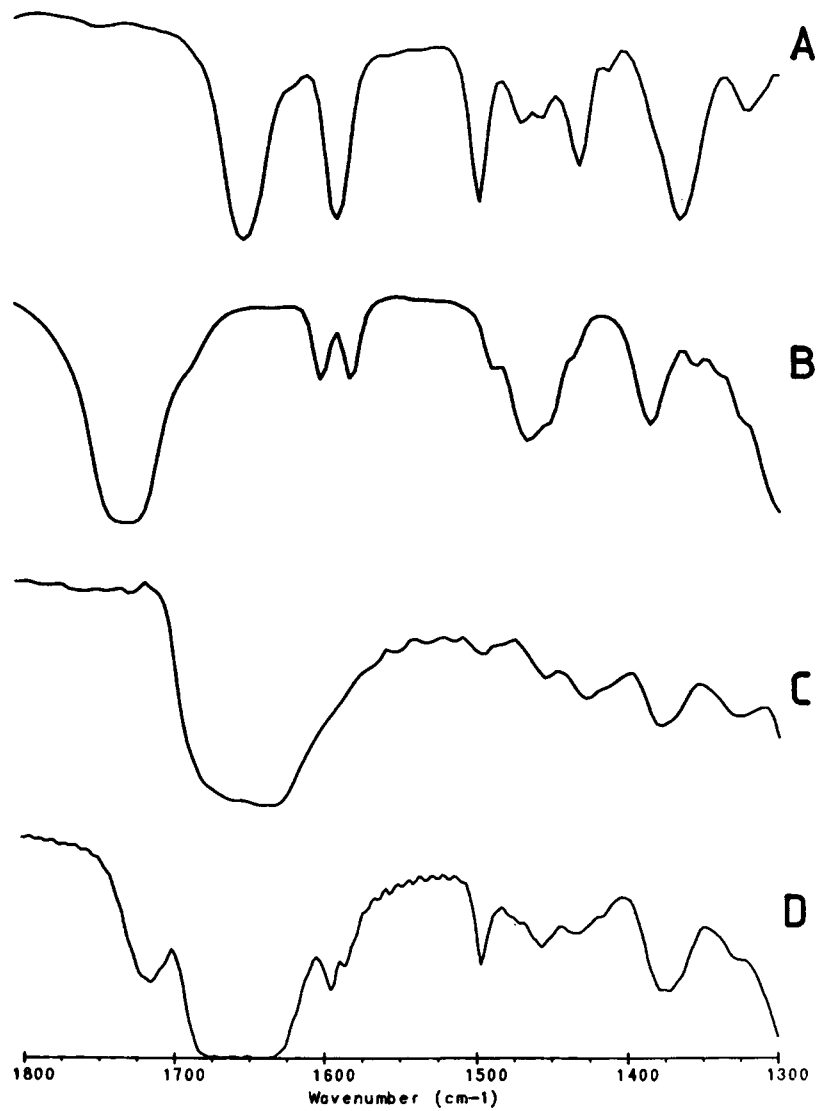
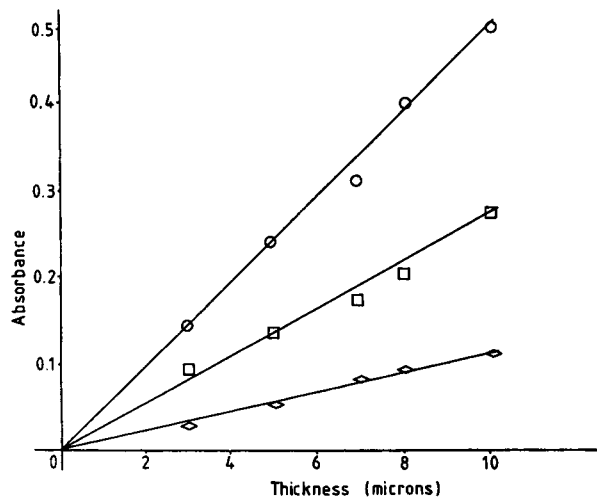


Figure 2 Reference IR spectra of (A) MC, (B) DBP, (C) NC base grain, and (D) MC/DBP deterred NC grain. Spectral range 1800–1300 cm^{-1} .



Propellants

The samples studied were of nitrocellulose grains deterred with methyl centralite (*N,N'*-dimethyl-*N,N'*-diphenyl urea) (MC) and dibutyl phthalate (DBP) in the same grains:

- A. NC deterred with A% MC/DBP,
- B. NC deterred with B% MC/DBP,
- C. NC deterred with C% MC/DBP,

where $A < B < C$.

Figure 3 Relationship between DBP 1717 cm^{-1} C=O absorbance, MC 1596 cm^{-1} C—C absorbance, and MC 1496 cm^{-1} C—C absorbance and section thickness.

Microtomy

Sections, 10 μm thick, of the grains were prepared using a Reichert 1050 microtome and glass knives. The propellant grains were clamped directly into the microtome chuck without embedding in any resin. Grains were microtomed to approximately two-thirds of their original length and then the 10 μm -thick section was taken for analysis by FTIR microscopy.

Infrared Microscopy

An Aire Scientific universal infrared (IR) microscope mounted on a Nicolet 510 Fourier-transform

spectrometer was used in this study. A medium-band MCT (HgCdTe) detector in the microscope gives high sensitivity in the 4000–600 cm^{-1} range. Propellant grain cross sections were placed on 15 mm-diameter KBr windows and IR spectra were taken at 10 μm intervals from the outer edge inward (external profile) and 10 μm intervals from the perforation edge inward (internal profile) by positioning the grain under the 10 \times 20 μm aperture using an Automatic Measuring Systems (AMS) Quick Step stepper motor-driven automatic sample stage programmed to move horizontally in 10 μm steps. The aperture was calibrated with a standard microcalibration slide. A 36 \times cassegrain mirror objective was

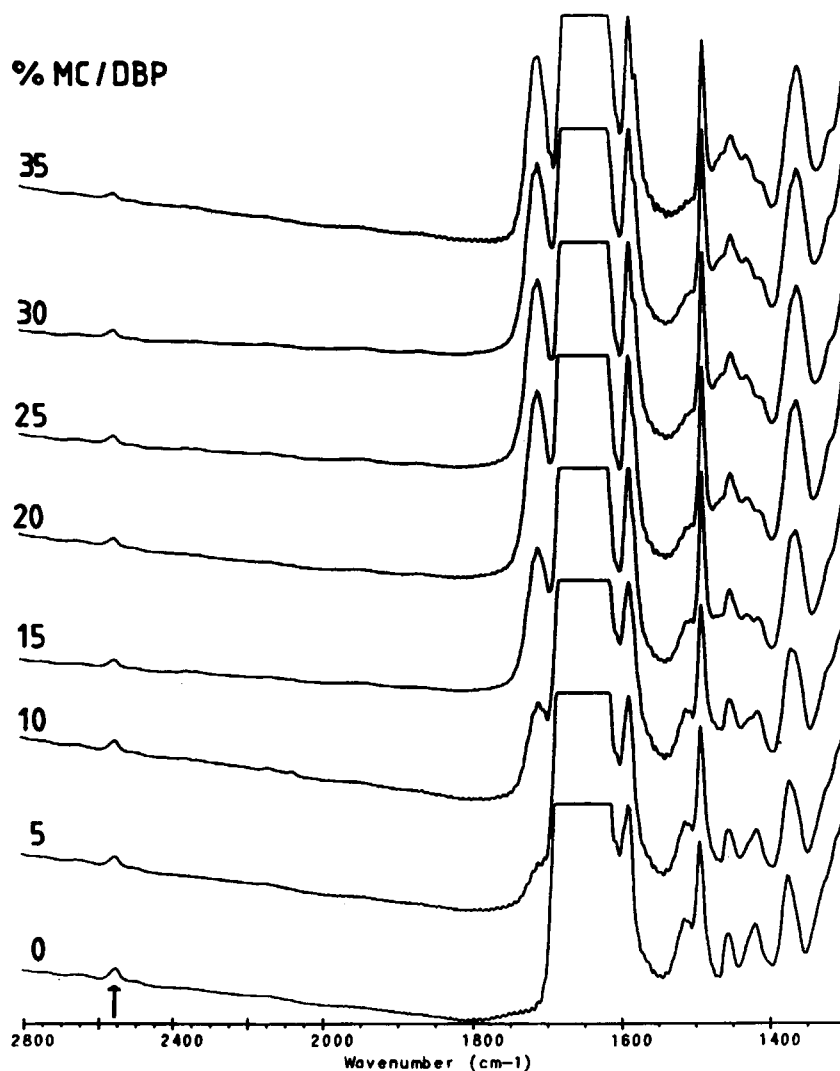


Figure 4 IR spectra of MC/DBP/NC calibration standards showing the —NO₂ overtone at 2555 cm^{-1} , DBP C=O at 1717 cm^{-1} , and MC 1596 and 1496 cm^{-1} aromatic C—C. Spectral range 2800–1300 cm^{-1} .

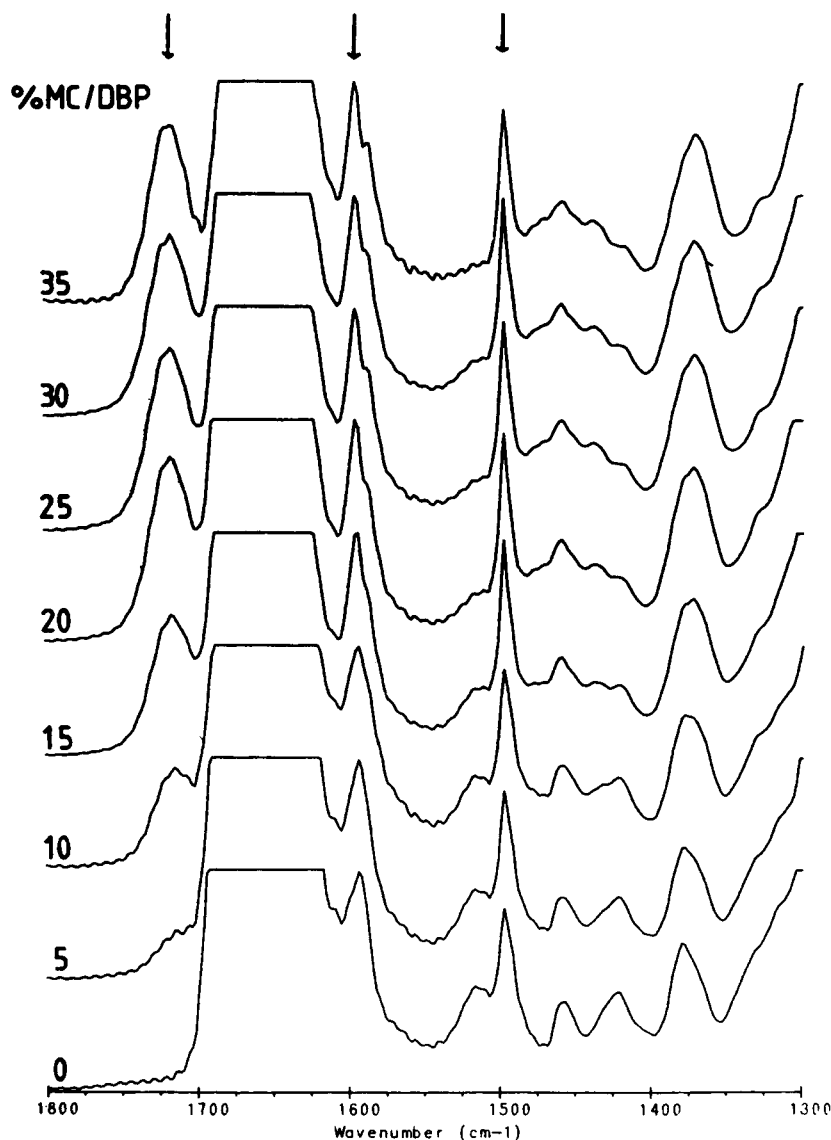


Figure 5 IR spectra of MC/DBP/NC calibration standards; spectral range 1800–1300 cm^{-1} .

used to obtain the infrared spectra. Infrared spectra were taken across the grain until no deterrent peaks were detected. The IR spectrometer was operated at a resolution of 8 cm^{-1} , zero filling once, and 1000 scans of each 200 square micron area were acquired.

Infrared Microimaging

Propellant grain cross sections were placed on 15 mm diameter KBR windows and IR spectra were taken through a $20 \times 20 \mu\text{m}$ aperture over a selected area in $20 \mu\text{m}$ steps. The IR spectrometer was operated at a resolution of 8 cm^{-1} . Two hundred fifty scans of each 400 square micron area were acquired.

RESULTS AND DISCUSSION

Method Requirements

The principal requirement in the development of an IR microscopy method for monitoring QUALITATIVE deterrent profiles into propellant powders is that the deterrent absorbs at a frequency where there is relatively little absorption by the matrix. Figure 1 shows IR reference spectra ($4000\text{--}650 \text{ cm}^{-1}$) of an MC/DBP deterred NC grain, MC, DBP, and an NC base grain. Figure 2 shows the same reference data over the range $1800\text{--}1350 \text{ cm}^{-1}$. It can clearly be seen that the carbonyl absorption band at 1717 cm^{-1}

Table I Absorbance of the DBP C=O and the MC Aromatic C—C Relative to the NO₂ Overtone of the NC

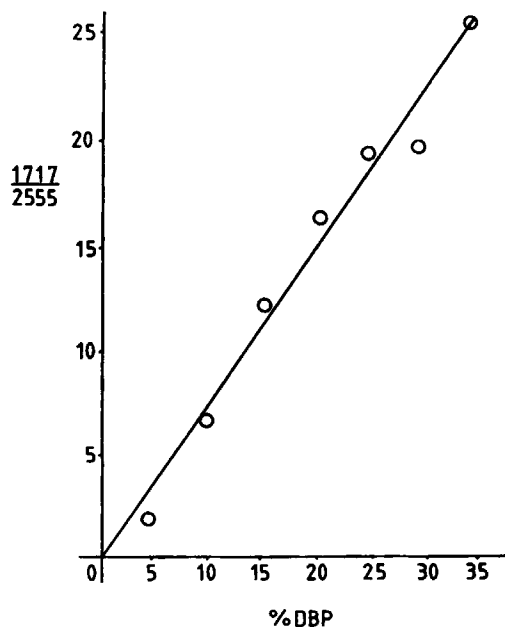
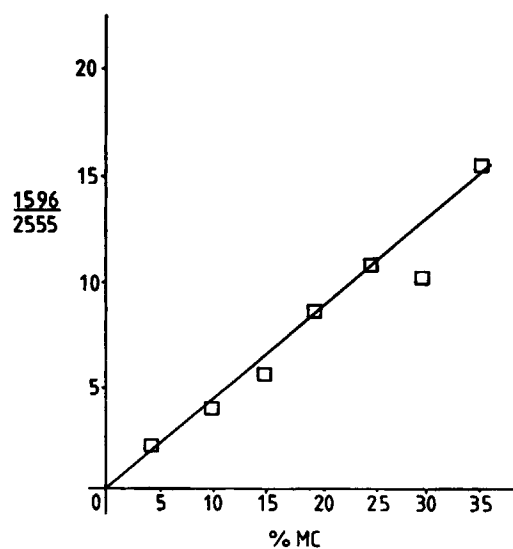
%MC/DBP	1717/2555	1596/2555	1596/2555 Corrected	1496/2555	1496/2555 Corrected
0	0.00	10.34		5.79	
5	1.30	12.36	2.01	7.77	1.98
10	6.50	14.11	3.77	9.53	3.74
15	11.79	15.60	5.26	11.37	5.58
20	19.09	20.40	10.06	15.13	9.34
25	19.29	21.08	10.74	15.66	9.88
30	19.21	19.73	9.39	14.81	9.02
35	25.42	25.90	15.56	19.25	13.46

of DBP and the aromatic C—C bands at 1596 and 1496 cm⁻¹ of MC can be used as indicator bands to monitor the deterrent profiles through the grain.

The principal requirement in the development of an IR microscopy method for monitoring QUANTITATIVE deterrent profiles into propellant powders is that the deterrent absorbs at a frequency where there is relatively little absorption by the matrix and that the matrix absorbs at a frequency where there is relatively little absorption by the deterrent. Figure 1 shows a peak in the base grain at 2555 cm⁻¹ (an overtone of the nitro vibration at 1250 cm⁻¹), which is absent from the MC and DBP reference

spectra. Consequently, measuring the absorption of the 1717 cm⁻¹ C=O of the DBP and the 1596 or 1496 cm⁻¹ aromatic C—C of the MC relative to the 2555 cm⁻¹ of the NC would give a quantitative measurement of the diffusion profiles.

Another important requirement of the IR method is that uniformly thick cross sections are used for the analysis. Absorbance values for the indicator bands 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 of DBP and the 1596 and 1496 cm⁻¹ bands of MC is shown in Figure 3. The relationship between absorbance and section thickness is seen to be linear at least to 10 μm. Consequently, 10 μm-thick cross section were used in this work.

**Figure 6** Calibration graph of I1717/I2555 cm⁻¹ vs. % DBP.**Figure 7** Calibration graph of I1596/I2555 cm⁻¹ vs. % MC.

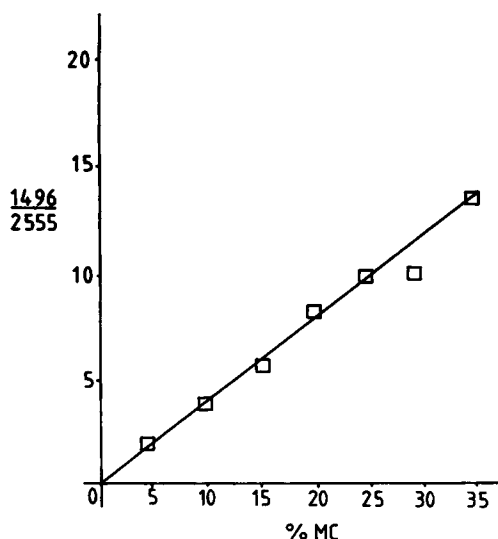


Figure 8 Calibration graph of I_{1496}/I_{2555} vs. % MC.

Calibration Standards

A series of calibration standards of MC/DBP in NC were prepared in the range 0–35% MC/DBP to NC w/w.

Figure 4 shows the IR spectra over the range $2800\text{--}1325\text{ cm}^{-1}$ for the calibration standards (top–bottom 35%–0%) and Figure 5 shows the same data over the range $1800\text{--}1325\text{ cm}^{-1}$. It can clearly be seen that the 0% MC/DBP standard contains no DBP but does contain an amount of MC—peaks at 1596 and 1496 cm^{-1} . This is because the calibration standards were prepared from a sample of NC containing an amount of MC and known weights of DBP/MC were added to obtain the standards. Table I shows the absorbance of the DBP $\text{C}=\text{O}$ and the MC aromatic $\text{C}-\text{C}$ relative to the NO_2 overtone of the NC.

Figures 6–8 show the linear calibration graphs of $1717/2555$ vs. % DBP, $1596/2555$ vs. % MC, and $1496/2555$ vs. % MC, respectively.

Penetration Depths

A total of six grains of each sample were analyzed and the penetration depths are shown in Table II. Penetration depths vary between the grains in the same sample for both the DBP and MC both externally and internally. In some cases, no DBP or MC

Table II Penetration Depth (microns)

Sample	Grain	External		Internal	
		DBP	MC	DBP	MC
A%MC/DBP	1	105	115	45	55
	2	95	105	35	45
	3	65	75	—	—
	4	95	95	35	45
	5	115	115	—	—
	6	75	75	25	35
Average		91	97	35	45
B%MC/DBP	1	115	125	30	35
	2	135	135	65	65
	3	105	115	85	85
	4	135	145	75	85
	5	125	135	—	—
	6	95	105	95	105
Average		118	127	70	105
C%MC/DBP	1	145	145	75	75
	2	165	175	105	115
	3	185	195	175	174
	4	165	175	75	75
	5	165	175	125	125
	6	165	175	115	115
Average		165	173	111	113

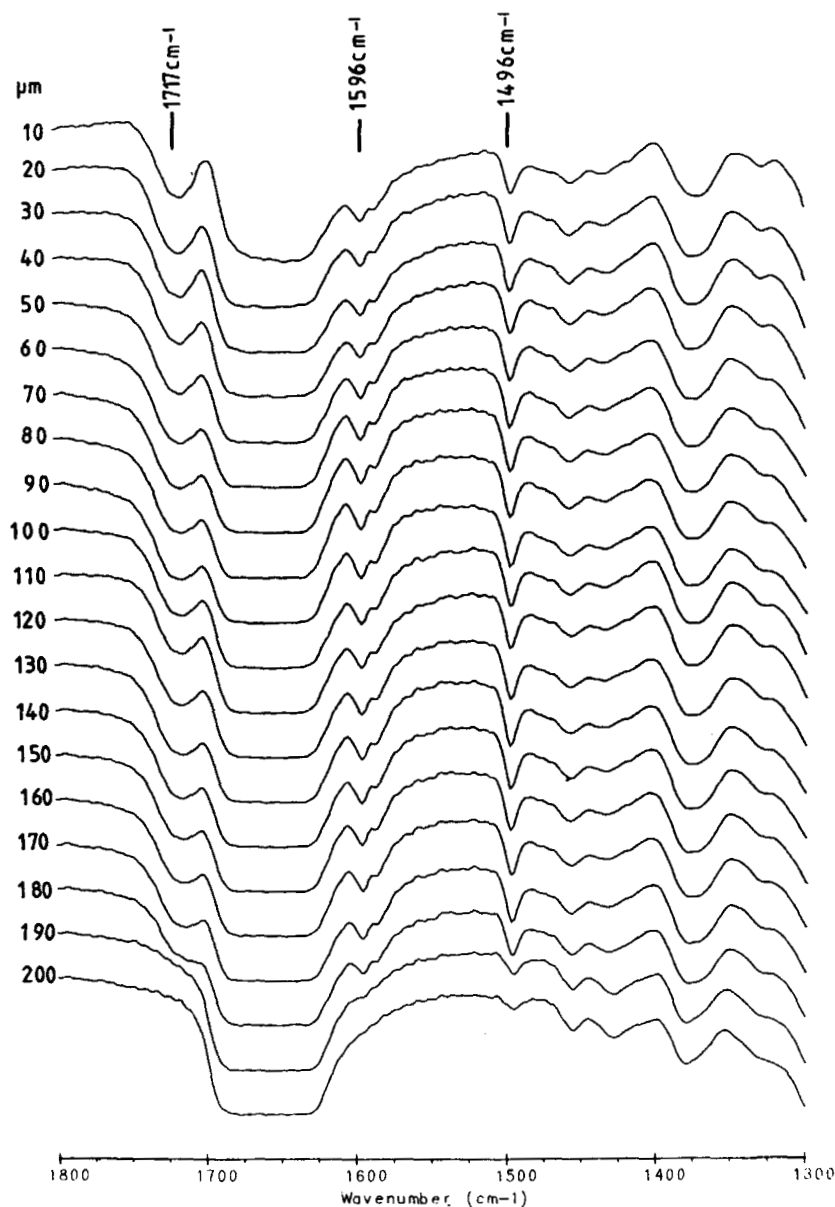


Figure 9 IR spectra of the external profile for a C% MC/DBP deterred grain.

was detected internally, possibly due to the perforation being blocked during the deterring process. Generally, the MC diffused further into the grain than did the DBP by 6–10 μm externally and 2–10 μm internally. The higher the loading of MC/DBP deterrent, the deeper the penetration of both DBP and MC.

Diffusion Profiles

Figures 9 and 10 show the IR spectra obtained at 10 μm intervals for a grain with a C% loading of

MC/DBP for the external and internal profiles, respectively, showing the decrease in the DBP C=O and the aromatic C—C peaks into the grain.

Figure 11(a) and (b) shows the comparison of the average external and internal diffusion profiles of DBP of the samples examined, respectively. Figure 12(a) and (b) shows the comparison of the average external and internal diffusion profiles of MC of the samples examined, respectively.

Generally, for the A% and B% MC/DBP deterred samples, the external profiles of the DBP and MC showed a fairly level deterrent concentration

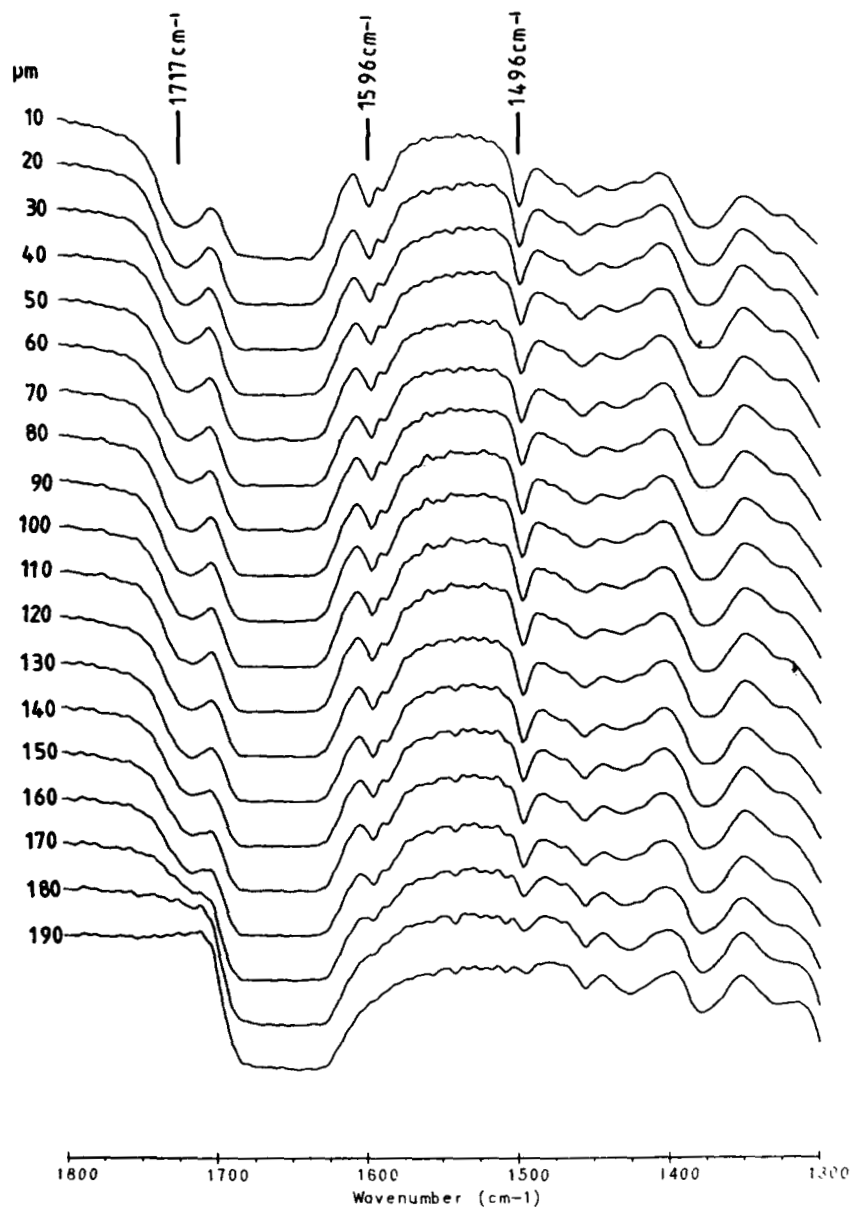


Figure 10 IR spectra of the internal profile for a C% MC/DBP deterred grain.

through a region of the grain followed by a gradual decrease in detergent concentration. The internal profiles generally showed a gradual decrease in concentration from the perforation edge inward.

For the C% DBP/MC deterred sample, the external profiles showed an initial increase in concentration to approximately $50 \mu\text{m}$, then a level concentration followed by a gradual decrease in concentration, and the internal profiles were a mixture of level concentration and gradual decrease and a rise in concentration followed by a gradual decrease.

The IR spectra taken in the deterred regions of

the grain showed a shift in the DBP C=O frequency to 1717 cm^{-1} in the nitrocellulose-based propellant compared with 1729 cm^{-1} in the spectrum of the detergent alone. Also, a shift was observed in the MC C—C frequency to 1596 cm^{-1} in the NC-based propellant compared with 1589 cm^{-1} in the spectrum of the detergent alone. These data suggest that a diffusion with the interaction process is occurring as hypothesized by Brodman et al.¹⁰

The detergent profiles indicate that detergent concentration and penetration depth varied from grain to grain within the samples, indicating non-

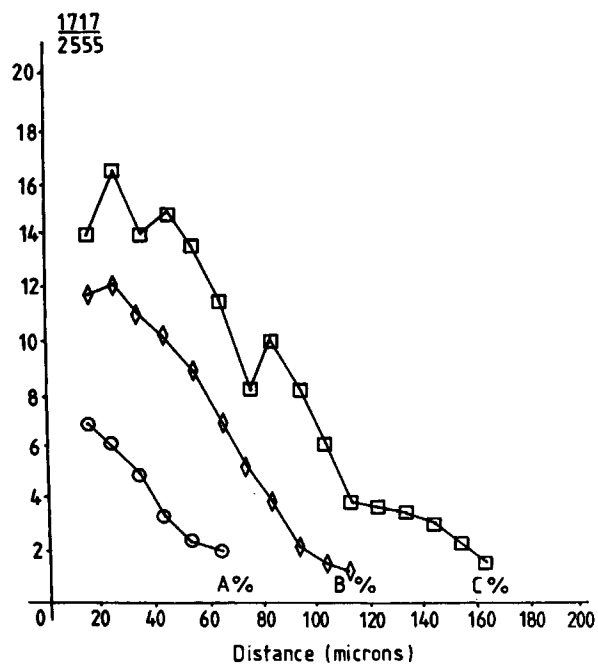
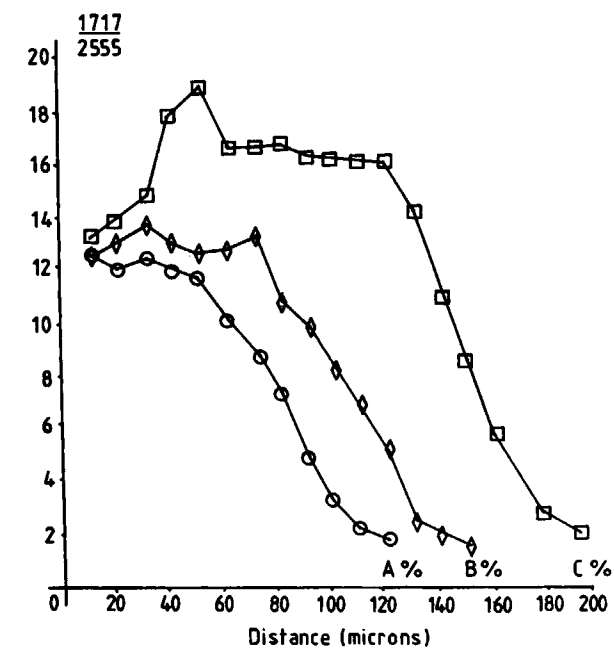


Figure 11 (a, b) Comparison of the average external and internal diffusion profiles of DBP for the three samples, respectively.

uniform coating of the grains. This is not unexpected due to the deterring method used.

Infrared Microimaging

Figure 13 shows the axonometric plot of the DBP distribution of an area 1×0.25 mm encompassing

the external edge and the central perforation of the cross section. It can clearly be seen that the DBP is highly concentrated at the external edge and around the central perforation. Figure 14 shows the axonometric plot of the MC distribution of the same area of the sample. The MC is highly concentrated at the

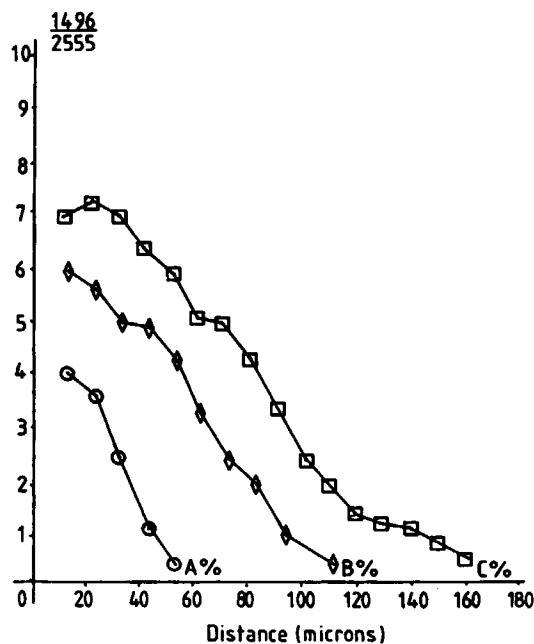
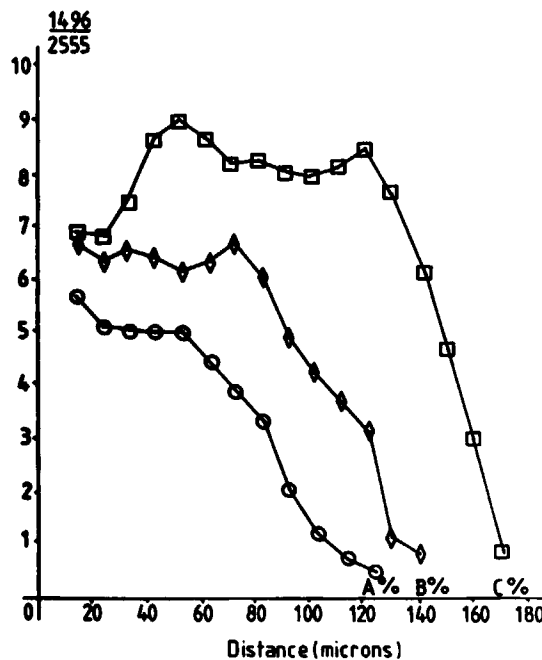


Figure 12 (a, b) Comparison of the average external and internal diffusion profiles of MC for the three samples, respectively.

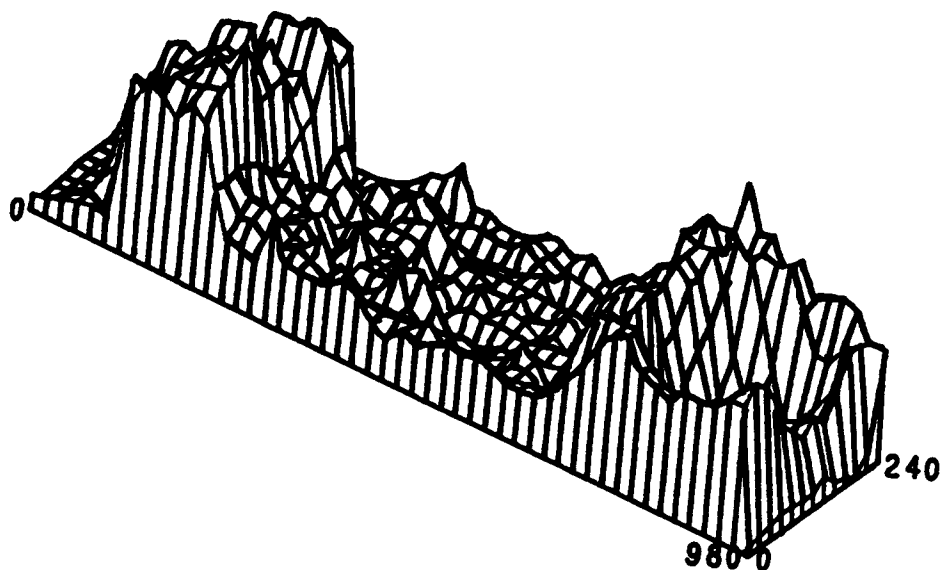


Figure 13 Axonometric plot of DBP (area 1×0.24 mm, step size 20 microns, aperture 20×20 microns), from external edge to central perforation of the propellant grain.

external edge and around the central perforation and occupies the same place as that of the DBP.

Figure 15 shows the axonometric plot of the DBP distribution of an area 0.6×0.44 mm at the external edge of the cross section. Figure 16 shows the axonometric plot of the MC distribution of the same area of the sample. These figures show the DBP and the MC to be in the same place at high concentrations.

Figure 17 shows the axonometric plot of the DBP distribution of an area 1×0.84 mm around the central perforation of the cross section. Figure 18 shows the axonometric plot of the MC distribution of the same area around the central perforation. These figures again show the DBP and MC occupying the same area and distributed around the central perforation in high concentration.

By selecting the appropriate spectra to be dis-

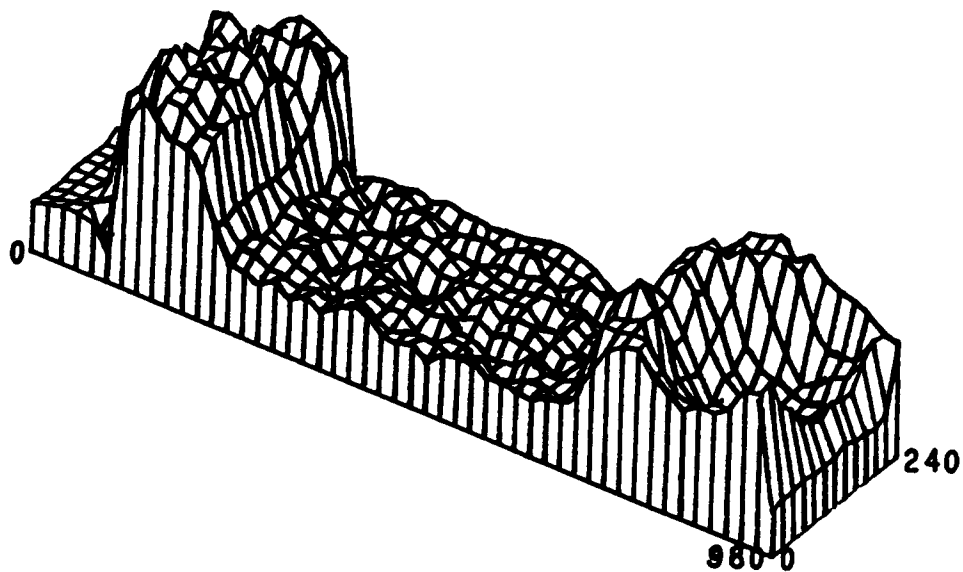


Figure 14 Axonometric plot of MC (area 1×0.25 mm, step size 20 microns, aperture 20×20 microns), from external edge to central perforation of the propellant grain.

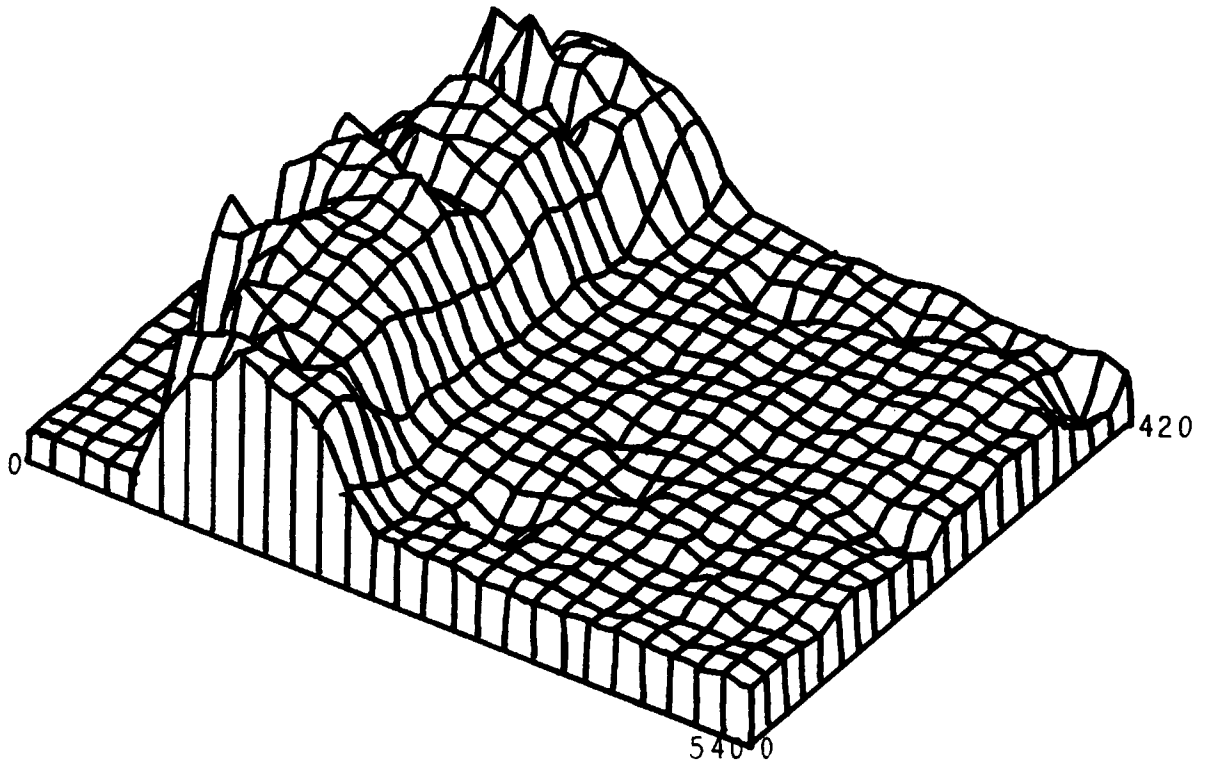


Figure 15 Axonometric plot of DBP (area 0.6×0.44 mm, step size 20 microns, aperture size 20×20 microns), at external edge of the propellant grain.

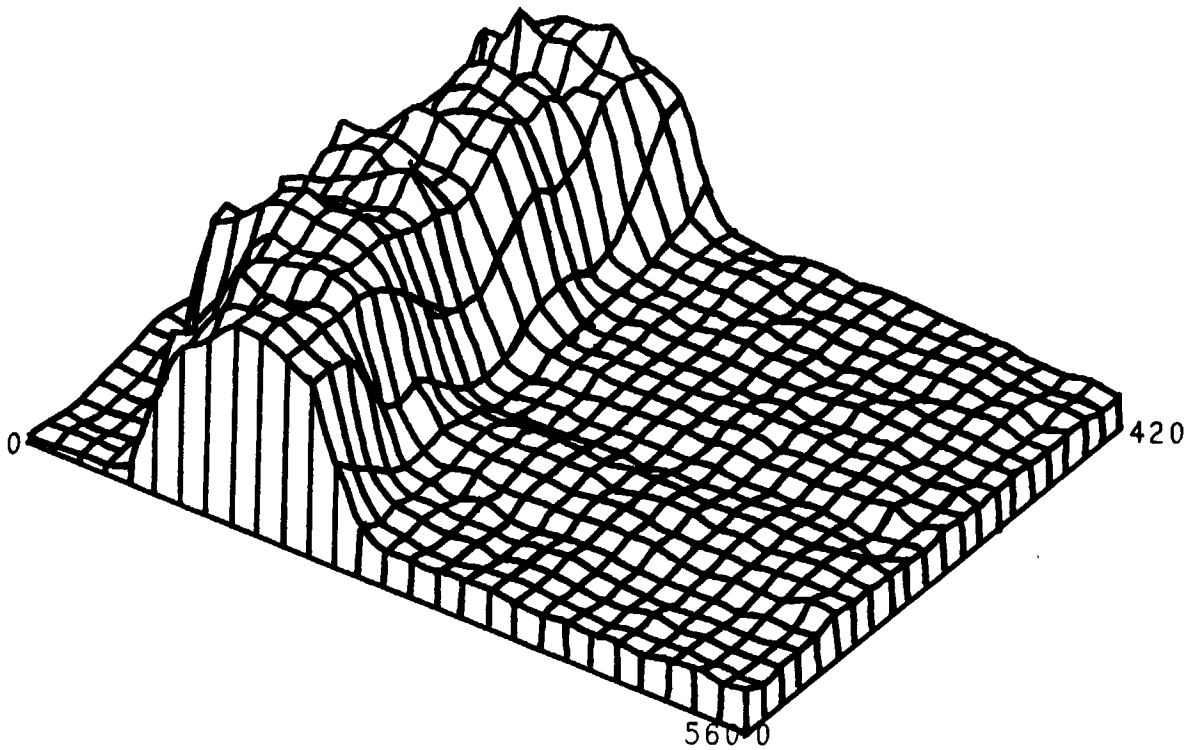


Figure 16 Axonometric plot of MC (area 0.6×0.44 mm, step size 20 microns, aperture size 20×20 microns), at external edge of the propellant grain.

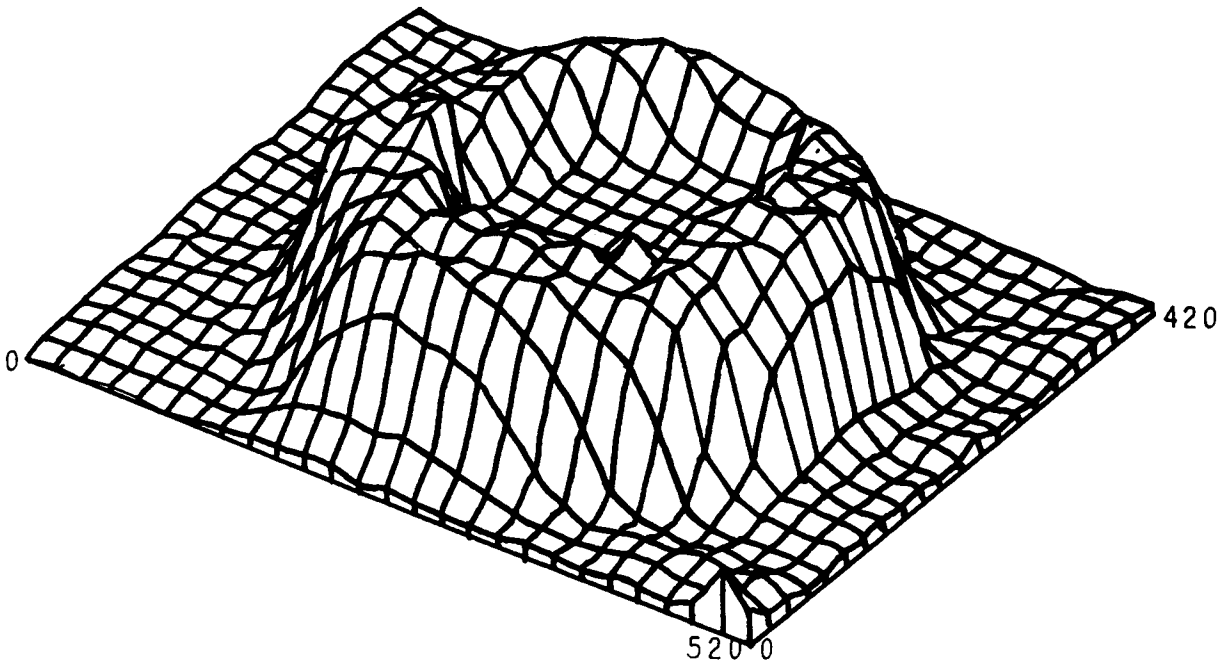


Figure 17 Axonometric plot of DBP (area 1×0.84 mm, step size 20 microns, aperture size 20×20 microns), around the central perforation of the propellant grain.

played, the diffusion profiles of the three areas can be easily plotted (Figs. 19–21). The scale on each of the figures is 20 microns per division and, consequently, the penetration depth is easily measured as is the shape of the diffusion profile.

CONCLUSIONS

Infrared microscopy is capable of providing qualitative and quantitative data on the concentration profiles and penetration depths of deterrents

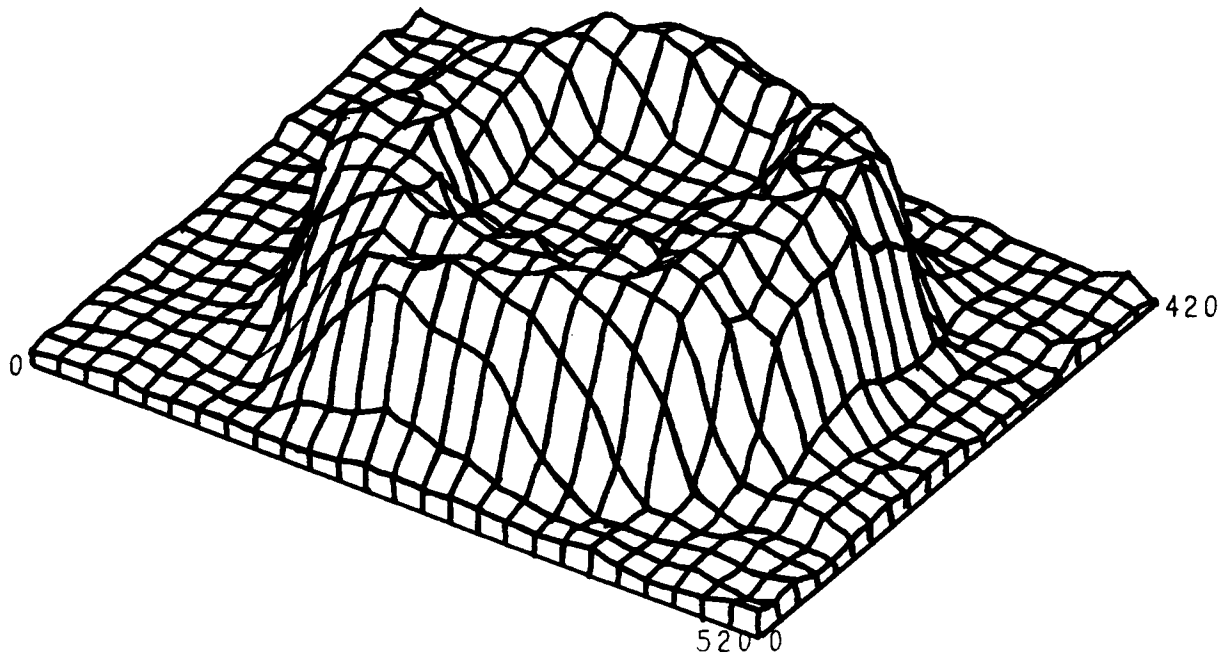


Figure 18 Axonometric plot of MC (area 1×0.84 mm, step size 20 microns, aperture size 20×20 microns), around the central perforation of the propellant grain.

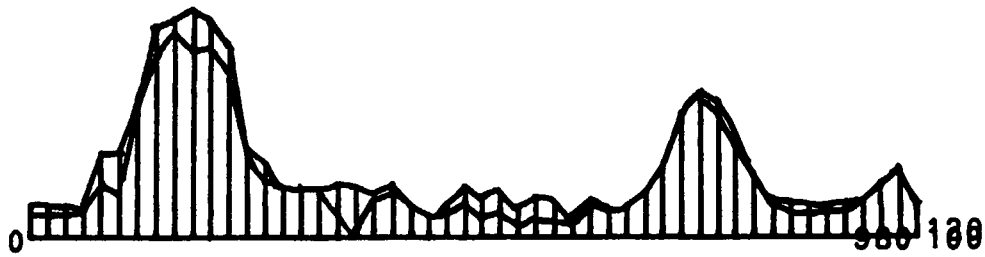


Figure 19 Diffusion profile from external edge to central perforation of the propellant grain.

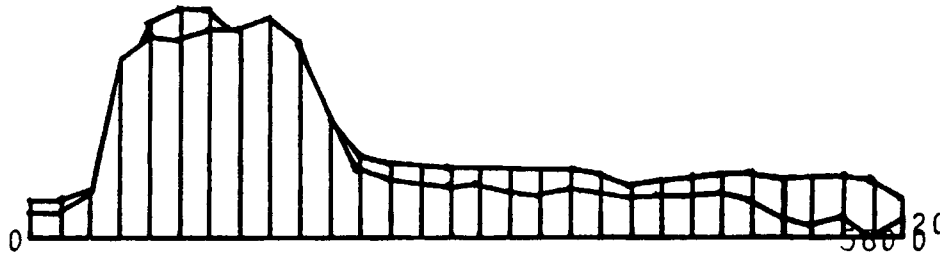


Figure 20 Diffusion profile from external edge of the propellant grain.

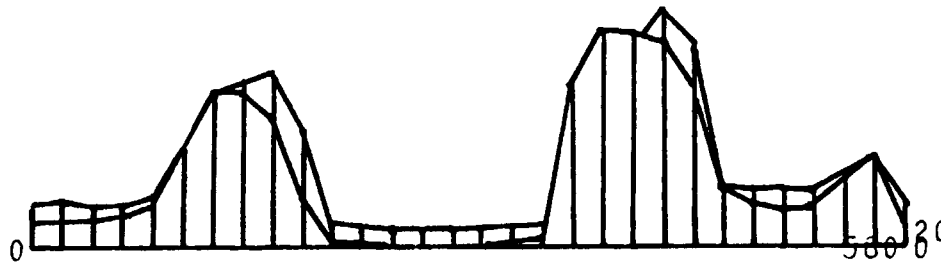


Figure 21 Diffusion profile of central perforation of the propellant grain.

(whether singly or multiply) diffused into single-based NC and double-based NC/NG matrix. The profiles obtained are consistent with Brodman's diffusion with interaction mechanism.

The higher the loading of deterrent, the greater the concentration and penetration depth in the grains. For the doubly deterred system studied here, the profiles of the MC and DBP are very similar.

The spatial resolution obtainable with the IR method is not as good as the spatial resolution obtainable with the Raman technique (1 micron). However, it is possible to obtain satisfactory signal-

to-noise spectra through a 5×20 micron aperture, giving an effective spatial resolution of 5 microns.

Infrared microimaging is capable of determining the distribution, penetration depth, and diffusion profile shape of deterred NC (in this case DBP and MC, but the method is equally applicable to other deterrents and double-based systems). The maximum practicable spatial resolution obtainable with the infrared microimaging method is approximately 10×10 microns.

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