

# Diffusion of Deterrents into a Nitrocellulose-Based Small Arms Propellant. The Effect of Deterrent Structure and Solvent

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## Synopsis

The depth of penetration of five urea-based deterrents and of dinitrotoluene into an extruded monoperoforated nitrocellulose propellant has been studied. The depth of penetration is directly proportional to the concentration of the deterrent solution. Structural variation of the urea-based deterrents and increasing the water content of the alcoholic deterrent solutions have significant effects on the depth of deterrent penetration. Dinitrotoluene penetrates more rapidly than the urea deterrents in all solvents studied. The results are consistent with a diffusion with interaction mechanism. It is suggested that some previous evidence for such a mechanism was not definitive.

## INTRODUCTION

Deterrents are compounds which are diffused into nitrocellulose-based small arms propellant grains in order to reduce the burning rate early in the ballistic cycle when the propellant bed surface area is large. The deterrents burn endothermically compared with the nitrocellulose matrix. Minor variations in the depth of penetration and concentration of deterrents in small arms propellants have been found to have a dramatic effect on the propellant's ballistic performance.

Established methods for measuring the depth of deterrent penetration into nitrocellulose propellant grains include various staining and optical techniques,<sup>1-5</sup> as well as autoradiographic<sup>2</sup> and scintillation counting<sup>5</sup> procedures. Examination of sectioned grains of extruded propellant under the optical microscope reveals the presence of distinct concentric regions due to the deterrent around the periphery of the grain and sometimes around the central perforation.<sup>1</sup> It is significant that the depth of the deterred region measured optically corresponds well with the depth measured by autoradiographic techniques.<sup>2</sup>

Brodman et al.<sup>2-4</sup> have suggested on the basis of measured concentration profiles of deterrent and infrared hydroxyl stretching frequency shifts that a diffusion with interaction mechanism best explains the observed depth of deterrent penetration into nitrocellulose matrices. It is envisaged that the deterrent moves into the propellant grain by diffusion and that molecules of the deterrent are removed from the diffusion stream by hydrogen bonding to the unnitrated hydroxyl groups of nitrocellulose. It has been generally found that the depth of the deterrent layer is linearly related to the deterrent concentration.<sup>1-5</sup> Quite different concentration profiles of deterrent have been observed for nitrocellulose propellants using different solvent systems,<sup>2,5</sup> suggesting that the observed level concentration of deterrent through the deterred region<sup>2</sup> is not a unique criterion for a chemical interaction accompanying diffusion. Similarly,

while correlations between infrared hydroxyl stretching frequency shifts of nitrocellulose and depth of deterrent penetration may exist, it does not necessarily follow that such correlations are good indicators of chemical interaction between the deterrent and nitrocellulose.

While it is difficult to predict what factors will influence the kinetic and thermodynamic aspects of a chemical interaction between a deterrent molecule and nitrocellulose, it is far easier to monitor the diffusion aspect of the penetration mechanism. The various theories of diffusion<sup>6</sup> in polymeric systems are based upon the creation of transient "holes" in the matrix resulting from molecular motion of the polymer network. Diffusion then results from molecular "jumping" among the dynamic distribution of "holes." Such concepts explain the well established effect of molecular size on the diffusion rate in polymers.<sup>6-8</sup> Hence from a knowledge of the molecular size of the deterrent it should be possible to monitor the diffusion part of the penetration mechanism.

Despite the number of studies on diffusion of deterrents into nitrocellulose propellants, there has been no systematic study of the effect of the "carrier" solvent. It is obvious that solvation of the deterrent and the active sites of nitrocellulose could have a major effect on the diffusion and interaction processes.

This study investigates the depth of deterrent penetration of five urea-based compounds and of dinitrotoluene into a monoperforated extruded nitrocellulose propellant using ethanol as a carrier solvent. The effect of structural variation of the urea-based deterrents as well as the influence of increased water content of the solvent upon the depth of penetration is used to gain further insights into the diffusion with interaction mechanism for deterrent penetration into nitrocellulose matrices.

## EXPERIMENTAL

The extruded monoperforated nitrocellulose propellant grains used in this study were undeterred AR2206 propellant<sup>9</sup> containing 2% water manufactured by Mulwala Explosives Factory. The moisture free nominal composition was diphenylamine 0.8–1.0%, dinitrotoluene (DNT) 4.0–8.0%, graphite 0.3%, potassium sulphate 0.3–0.8%, potassium nitrate 0.1%, and the remainder nitrocellulose (NC) 13.15% N. The mean length of the grains was 1.5 mm, the mean web 0.3 mm, and the maximum perforation diameter 0.14 mm.

The coating procedure was as follows: 20 g of propellant was added to the required weight of the deterrent dissolved in 24 g of solvent; the deterrent solution was previously stored for 1 h at 63°C; the reaction flask was attached to a rotary evaporator under reflux conditions and rotated for 1 h at 63 ± 2°C; the solvent was removed under vacuum (15 mm Hg, 60–90°C) at the end of this period and finally dried in a vacuum oven at 65°C, ca. 1 mm, 1 h; these conditions have been shown to result in the essentially quantitative transfer of deterrent to the propellant grains (by weighing the residual deterrent in the reaction flask). The solvents used were 95% ethanol (EtOH), EtOH:H<sub>2</sub>O (1:1, w/w), and EtOH:H<sub>2</sub>O (1:2, w/w).

The deterrents used were (a) diphenyl urea (DPU), (b) *N,N'*-dimethyl *N,N'*-diphenyl urea, or methyl centralite (MC), (c) *N,N'*-diethyl *N,N'*-diphenyl urea, or ethyl centralite (EC), (d) *N,N'*-diethyl *N*-4-chlorophenyl *N*-phenyl urea (DECPPU), (e) *N*-4-chlorophenyl *N*-phenyl thiourea (CPPTU), and (f) 2,4-

dinitrotoluene (DNT). All compounds were pure as adjudged by physical constants, elemental analysis, or spectroscopic criteria.

The applied deterrent solutions varied from 0% to 7.5% (w/w). A minimum of five concentrations were used, though most studies utilized six or seven concentrations.

The sectioned grains were examined using a Zeiss Ultraphot 2 calibrated microscope with polarized light at magnifications varying from 30 to 50. Specimen sections for microscopy were cut with a microtome from grains held in polythene (ca. 25  $\mu$  thick) or were cut manually with a fresh razor blade. Both techniques gave consistently similar results for depth of penetration. The depth of penetration was the average of five individual sections with the error being  $\pm 5 \mu$ . The average values were corrected to the average diameter of the grains to avoid grain-to-grain variation. Sections were taken from a position a quarter of the distance along the length of the grain.

## RESULTS AND DISCUSSION

Microscopic examination of grain sections revealed distinct concentric regions around the periphery and the central perforation, with the latter region being smaller in area. Independent evidence that these regions did, in fact, correspond to the deterred regions was confirmed from the energy dispersive X-ray scattering spectrum (scanning for Cl at 2.621 eV,  $K_{\alpha 1}$ ) obtained from scanning electron microscopy of grain sections coated with DECPPU and CPPTU. The peaks were observed in the EDAXS spectrum which corresponded with the outer and inner deterrent bands observed with the optical microscope. Unfortunately, the original intention to quantify the concentration gradient of deterrent in these bands was not realized owing to sensitivity and specimen surface effects.

In order to remove geometric effects, the depth of penetration of the bands has been calculated as the area of the deterred region (corrected for grain-to-grain variation in diameter and web size). The variation in depth of penetration was found to be directly proportional to the concentration of the applied deterrent solution. Since it was confirmed from control experiments utilizing the three solvents alone that zero-deterrent concentration gave no observable bands under the optical microscope, the least-squares equation (1) relating concentration to the depth of penetration was force fitted through the origin:

$$\text{concn} = b(\text{area of deterrent band}) \quad (1)$$

The inverse of the proportionality factor  $b$  is a direct measure of the relative penetrating ability of the various deterrent-solvent systems. The proportionality factors are given with their 95% confidence limits in Table I.

Inspection of the proportionality factors reveals that the values for the outer band for the various deterrent/solvent systems are mirrored by the corresponding values for the inner band, though the latter are of a much reduced magnitude. This observation is good evidence that the same mechanism for deterrent penetration operates at the outer and inner surfaces of the grain, but with diffusion into the area around the perforation reduced owing to restricted access of the deterrent solution into the perforation.

DNT, the current commercial deterrent used with AR2206 propellant, is chemically quite different from the urea-based deterrents. It is less polar and has a weaker hydrogen bond ability<sup>10-12</sup> and is also overall sterically smaller than

TABLE I  
Proportionality Factors and Their 95% Confidence Limits for Various Deterrents

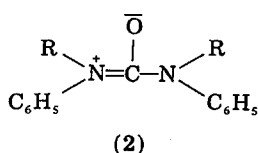
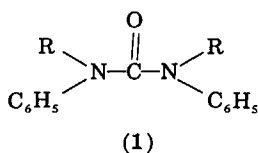
Solvent	Deterrent					
	DPU	MC	EC	DECPPU	CPPTU	DNT
EtOH <sup>a</sup>	22.6 ± 1.5	26.3 ± 4.6	20.5 ± 4.1	26.2 ± 6.3	24.7 ± 5.5	18.3 ± 4.6
EtOH/ H <sub>2</sub> O; 1:1 <sup>a</sup>		17.8 ± 2.4	26.9 ± 5.6	35.1 ± 14.6		19.0 ± 4.1
EtOH/ H <sub>2</sub> O; 1:2 <sup>a</sup>		31.5 ± 9.7	24.9 ± 8.0	27.1 ± 14.7		21.8 ± 5.8
EtOH <sup>b</sup>	291.8 ± 62.7	383.1 ± 116.6	309.9 ± 68.8	401.9 ± 75.4	357.0 ± 66.8	164.9 ± 71.1
EtOH/ H <sub>2</sub> O; 1:1 <sup>b</sup>		384.9 ± 63.3	416.9 ± 141.9	523.9 ± 106.3		199.5 ± 64.1
EtOH/ H <sub>2</sub> O; 1:2 <sup>b</sup>		361.8 ± 63.3	308.5 ± 49.1	348.6 ± 47.1		209.4 ± 82.5

<sup>a</sup> Outer band (around periphery).

<sup>b</sup> Inner band (around perforation).

the urea-based deterrents, as predicted from steric substituent constants.<sup>13</sup> All three factors would be expected to result in a much greater penetrating ability for DNT than for the urea-based deterrents in all solvents, assuming a diffusion with interaction mechanism is operative. Inspection of Table I (the reciprocals of the proportionality factors) reveals that such a prediction does in fact occur.

The proportionality factors for the urea-type deterrents indicate that molecular structure and the solvent both have a significant effect on the depth of penetration. Comparisons among DPU, MC, and EC in EtOH reveal that substitution of the amino-hydrogen atom by N—Me and N—Et groups, respectively, causes significant\* changes to the proportionality factors. Such changes may be attributed to variations in the chemical interaction between the deterrent and the NC matrix resulting from increased contribution of canonical form (2) to the resonance hybrid (thereby increasing polar and hydrogen bonding



properties of the deterrent). It seems reasonable to assume that the various urea-type deterrents are very similar in overall steric size in view of the much greater steric size of the benzene rings<sup>13</sup> compared to the R groups. However, while increased polarity and hydrogen bonding ability of these deterrents de-

\* When comparing two proportionality factors and their associated 95% confidence limits, overlap of the confidence limit ranges does not mean that significant differences between the proportionality factors do not exist. Differences between the factors can be tested using a pooled *t* test procedure.<sup>14</sup> Such comparisons reveal that the reciprocals of the proportionality factors for DNT are significantly greater at the 95% level than the majority of the corresponding factors for the urea-based deterrents.

crease in the order  $EC > MC > DPU$ , and the thermodynamic stability of the interactions with NC would be expected to decrease in the same order, the increase in steric size<sup>13</sup> of the R group may affect the kinetic aspects of the deterrent—NC interaction in a complex fashion.

DECPPU in EtOH unexpectedly shows a significant difference from EC in EtOH as adjudged from a comparison of their proportionality factors, considering that the only structural difference is that DECPPU possesses a 4-chloro atom on one benzene ring instead of a hydrogen atom. It is possible that the 4-chloro atom increases the contribution of canonical form (2) to the resonance hybrid. There appears to be no significant difference between DPU and CPPTU in EtOH. While CPPTU is sterically larger than DPU, the greater polarizability of the sulphur atom would reduce its hydrogen bond donor ability relative to the carbonyl oxygen atom.

It would appear from the proportionality factors for the five urea-based deterrents in EtOH that small structural changes can induce significant variations in the degree of chemical interaction between the deterrent and the NC matrix.

Comparison of the proportionality factors for MC, EC, DECPPU, and DNT indicate that increasing the water content of the solvent has a major effect on the penetrating power of the urea-type deterrents but an insignificant effect on that of DNT. Increasing the polarity of the solvent will lead to an increased contribution of canonical form (2) to the resonance hybrid of the urea-based deterrents<sup>12</sup> and consequently result in a tight inner solvation shell of water molecules. As a result, there will be a decreased penetrating ability of the urea deterrents owing to increased polar and hydrogen bonding interaction of the deterrent molecules with the NC and to the increased effective steric size of the strongly solvated deterrent molecules. DNT will not show as great a sensitivity to increased solvent polarity<sup>10,11</sup> as the urea deterrents, and therefore the depth of penetration of DNT in solvents of increasing water content should be much less affected, which is exactly as observed.

The proportionality factors of MC, EC, and DECPPU indicate major changes in the depth of deterrent penetration as the proportion of water increases in the solvent. MC is the most sensitive of the urea-based deterrents to solvent changes, actually increasing in depth of penetration in EtOH:H<sub>2</sub>O (1:1) but decreasing significantly in EtOH:H<sub>2</sub>O (1:2), as anticipated from the above arguments. The increase in penetration in EtO:H<sub>2</sub>O (1:1) compared to that in EtOH is difficult to explain and is the one anomaly to the general rule that the depth of penetration of the urea deterrents becomes less as the concentration of water in the EtOH:H<sub>2</sub>O solvent increases. EC penetrates less in EtOH:H<sub>2</sub>O (1:1) than it does in EtOH, but penetration is relatively unaffected as the concentration of water in the solvent is further increased. DECPPU appears to show no significant changes in penetration as the water concentration is increased, but the statistical precision in these cases is the worst in the study. The sensitivity and differential behavior of these urea deterrents to solvent effects are strong evidence of the importance of chemical interactions in determining the depth of deterrent penetration.

Both structural effects and solvent effects can have a major influence on the depth of deterrent penetration into NC matrices. The observed proportionality factors are consistent with the previously postulated<sup>2-4</sup> diffusion with interaction mechanism. However, we would urge caution in assuming that correlations

between the depth of deterrent penetration and infrared shifts of the hydroxyl stretching frequencies of NC are definitive evidence of the chemical interaction part of the diffusion with interaction mechanism.<sup>2-4</sup> For example, Brodman et al.<sup>4</sup> have observed such a relationship for four alkyl esters of benzoic acid. While it may be argued that four data points give little indication of the validity of the relationship, it should be pointed out that the increasing steric size of the methyl, ethyl, *n*-propyl, and *n*-butyl benzoates is inversely related to the decreasing depth of penetration of these compounds. Meier et al.<sup>5</sup> have also noted that the rate of penetration of dibutyl phthalate into a NC matrix is faster than for dioctyl phthalate, which is consistent with the larger steric size of the latter deterrent. Interestingly, it was noted that both phthalates migrated less rapidly when applied in an ethanol solution than they did when applied in a propanol solution.

The decrease in penetrating ability of the benzoates<sup>4</sup> and phthalates<sup>5</sup> as they increase in steric size is consistent with a change in diffusion behavior, while the observed solvent effect for the phthalates implies a change in chemical interaction.

Thus, it seems pertinent to point out that in searching for evidence of a chemical interaction accompanying diffusion in polymeric systems, it is necessary to differentiate between thermodynamic stability and kinetic control of such chemical interactions.

We are currently developing a theoretical model for this system based upon a consideration of steric size of the deterrent and solvent molecules (diffusion aspect) and measures of the chemical interaction between the various molecular species and nitrocellulose. Such a model should be of considerable help in clarifying the results obtained in this study.

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