

The Non-Fickian Diffusion of Deterrents into a Nitrocellulose-Based Propellant

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Synopsis

The diffusion of solutions of ethyl centralite (EC), dibutylphthalate (DBP), and dinitrotoluene (DNT) into a nitrocellulose (NC) propellant is investigated. DBP and EC penetrate the propellant in a way consistent with Case II diffusion. The diffusion of DNT solutions is Fickian. The apparent activation energy for Case II diffusion is 62 kJ/mol for DBP and 66 kJ/mol for EC. Changes to coating solvent polarity have little effect on DNT and DBP penetration and merely alter the rate, not the mechanism, of EC diffusion into the propellant.

INTRODUCTION

Diffusion of low molecular weight, endothermic materials into the outer layers of a granular, energetic, polymeric material, such as nitrocellulose, is very important in controlling the burning rate of gun propellants early in the ballistic cycle. This control of the burning rate is necessary in tailoring ballistic performance.¹ These low molecular weight materials, commonly called deterrents or moderants, are often good plasticizers for the polymer material.

The diffusion of deterrents into nitrocellulose propellants has been studied by several workers, and has also been reviewed by Levy.² The radial concentration profile has been observed to be stepwise (i.e., a steep concentration gradient separates an inner core containing no deterrent from an outer band which has an approximately uniform deterrent concentration).³⁻⁵ A number of possible diffusion mechanisms can give rise to this type of concentration profile and several models have been proposed to describe this behavior.⁶

Brodman et al.⁷⁻¹¹ studied the molecular interactions between deterrents and the NC matrix and proposed a diffusion with interaction model to account for the observed concentration profiles. His model was proposed on the basis of shifts in the hydroxyl stretching frequency of NC in the infrared due to interaction between the deterrent and the unesterified hydroxyls on NC, although the influence of matrix and solvent effects cannot be discounted in Brodman's experiments. The diffusion with interaction model per se, is insufficient to yield the observed concentration profiles in any case. If hydrogen bonding (or indeed any other interaction such as dipolar) between the NC hydroxyls and the deterrent is such that there is an equilibrium set up

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between the free and bound detergent then

$$C_b = K C_f$$

where C_f is the concentration of free detergent and C_b is the concentration of detergent bound to the polymeric NC matrix and K is the equilibrium constant. This is the linear adsorption isotherm. Substituting this into the one-dimensional form of the diffusion equation,¹²

$$\partial C_f / \partial t = D \partial^2 C_f / \partial^2 x - \partial C_b / \partial t$$

yields an equation of the form

$$\partial C_f / \partial t = (D/K + 1) \partial^2 C_f / \partial^2 x$$

which is the "normal" Fickian diffusion relationship, except that the diffusion coefficient is reduced by a factor of $K + 1$. The concentration versus distance profile would be quite different from that observed, as described by Crank.¹² Many workers have studied diffusion in glassy and rubbery polymers and have classified diffusion behavior into three classes distinguished by the relative rates of diffusion and relaxation of the polymer matrix.¹²

1. *Case I or Fickian diffusion* in which the rate of diffusion is much less than the rate of relaxation. These systems are controlled by the diffusion coefficient and are characterized by a relationship between the fractional amount of material sorbed M/M_∞ and time of the form

$$M_t/M_\infty = k_1 \sqrt{t}$$

where M_∞ the amount absorbed at infinite time and k_1 is a proportionality constant.

This behavior is often seen in rubbery polymers (i.e., above T_g).

2. *Case II diffusion* in which the rate of diffusion is much greater than the rate of relaxation of the polymer. These systems are characterized by an advancing front in the matrix which moves at constant velocity and marks the boundary between a swollen gel and glassy core. The relationship between the amount taken up and time in this case is linear

$$M_t/M_\infty = k_2 t$$

3. *Non-Fickian or anomalous diffusion* which occurs when the diffusion and relaxation rates are comparable. The relationship between uptake and time in this case is intermediate between Case I and Case II

$$M_t/M_\infty = k_3 t^n$$

where n is between 0.5 and 1 or changes sigmoidally from one to the other. Nitrocellulose in propellants exists in a glassy state and a more likely mechanism for the observed concentration profiles than that proposed by Brodman is the occurrence of Case II diffusion due to swelling of the outer layer of the

cylindrical propellant grain under the influence of the deterrent. Such behavior is commonly observed in polymer diffusion experiments when the polymer is "glassy" (i.e., below its glass transition temperature T_g).

This study investigates the diffusion behavior of commonly used deterrents in single-base nitrocellulose propellant. The effect of temperature, coating solvent type, and deterrent type on diffusion rate and mechanism is investigated.

EXPERIMENTAL

The propellant used was an extruded, perforated single-base powder designated AR2206,¹³ manufactured at the Mulwala Explosives Factory and not deterrent coated. The propellant grains consisted of monoporate cylinders with mean length 1.50 mm, mean outer diameter 0.74 mm, mean inner perforation diameter 0.14 mm yielding a mean wall thickness or web of 0.30 mm. The nominal composition of the propellant was diphenylamine 0.8–1.0%, dinitrotoluene (DNT) 4.0–8.0%, graphite 0.3%, potassium sulfate 0.3–0.8%, potassium nitrate 0.1%, water 2%, and the remainder nitrocellulose (NC) nitrated to 13.15% N. The manufacturing process produces grains containing induced porosity.

The deterrents used were *N,N'*-diethyl *N,N'*-diphenylurea or ethyl centralite (EC), dibutyl phthalate (DBP), and 2,4-dinitrotoluene (DNT). The solvents used were ethanol and ethanol/water (2:1 v/v). Attempts were made to use an ethanol/water (1:1 v/v) solvent but deterrent solubility problems were encountered. These solvents were chosen because they are good solvents for the deterrents chosen and are similar to those used in the commercial coating of propellants. In addition they are relatively inert to nitrocellulose as McBain et al.¹⁴ have shown. This was identified as an important factor in the studies of the diffusion of acetone solutions into nitrocellulose conducted by Campbell and Johnson.¹⁵

The diffusion experiments were carried out using a modification of the factory propellant-coating procedure. First, 20.0 g of propellant was added to 250 mL of deterrent solution (prewarmed to the appropriate temperature) in a rotary evaporator flask. The mixture was tumbled at a slow rate, sufficient to prevent grains adhering to each other, with the solvent refluxing. At 5.0 min intervals accurately weighed 1 g samples of propellant were withdrawn, pat dried, and cooled. After 30.0 min, samples were removed every 10.0 min until at 120.0 min the experiment ceased. Temperatures were held constant by use of a water bath in which the rotary evaporator flask was immersed. This procedure ensured that the concentration of the solution remained effectively constant during the experiment.

The sampled grains were subjected to dichloromethane extraction analyzed for deterrent content using gas chromatography. The chromatograph was a Perkin Elmer Sigma 1 with flame ionization detector and a 3% OV 101 on Chrom WHP Mesh 100-120 column. Diethyl sebacate was used as an internal standard.

The depth of penetration of the deterrent in the grain was measured microscopically using annular cross sections of the grains obtained by use of a microtome. Sections were chosen from a position one quarter of the distance

along the grain longitudinal axis. The grain sections were examined using a Zeiss Ultraphot 2 calibrated microscope using polarized light. The depth of penetration was obtained as an average of values from five individual sections, with the standard deviation being approximately 10 μm . The bands observed by this method have been shown to correspond to deterred regions in previous studies utilizing autoradiography³ and energy-dispersive x-ray scattering.¹⁶

RESULTS AND DISCUSSION

Ethanol Solvent

The diffusion of 10% solutions of the deterrents EC, DBP, and DNT in ethanol was studied to gain an understanding of the diffusion mechanisms which apply to this system.

The relationship between amount of deterrent absorbed and contact time was investigated to obtain information on whether Case I (Fickian) or Case II diffusion mechanisms applied or whether it was necessary to consider intermediate case, non-Fickian or anomalous diffusion mechanisms. The deterrent uptake to the point where complete penetration through the propellant grain occurred was considered. A very approximate estimate of the penetration time can be obtained from the metrology data. The penetration of deterrent from the inner perforation was usually one half of that from the outer surface of the grain and this resulted in complete penetration at times corresponding to 200 μm penetration from the outer surface.

Shankar¹⁷ has provided an alternative and independent method of assessing the point where the two advancing boundaries meet and consequently the time for complete penetration of the grain. Plotting $\ln(1 - M_t/M_\infty)$ versus time yields a linear plot showing a sharp break in slope at the point where the boundaries meet. Shankar showed that this technique was applicable to sorption data from "non-Fickian" as well as Fickian systems. Although his method was derived for sorption into thin films an analogous situation applies to hollow cylinders. Crank¹² gives the relationship between fractional uptake and time for cylinder having outer radius b and inner radius a as

$$M_t/M_\infty = 1 - \frac{4}{(b^2 - a^2)} \sum_{n=1}^{\infty} \frac{J_0(a\alpha_n) - J_0(b\alpha_n)}{\alpha_n^2 (J_0(a\alpha_n) + J_0(b\alpha_n))} \exp(-D\alpha_n^2 t)$$

where the α_n are positive roots of

$$J_0(r\alpha_n)Y_0(b\alpha_n) - J_0(b\alpha_n)Y_0(r\alpha_n)$$

and J_0 and Y_0 are Bessel functions of the first and second kind, respectively, of order zero. The series converges rapidly and may be approximated by the first term

$$1 - M_t/M_\infty = \frac{4}{(b^2 - a^2)} \frac{J_0(a\alpha_1) - J_0(b\alpha_1)}{\alpha_1^2 (J_0(a\alpha_1) + J_0(b\alpha_1))} \exp(-D\alpha_1^2 t)$$

Consequently, a plot of $\ln(1 - M_t/M_\infty)$ vs t will be linear as Figures 1 to 3

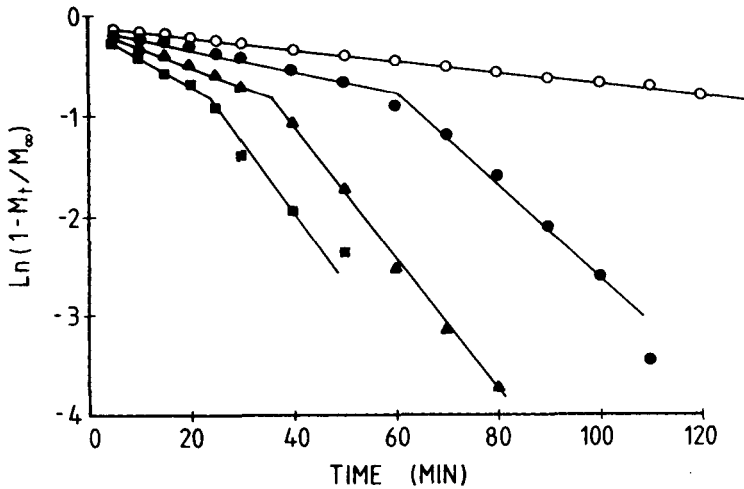


Fig. 1. Sorption of DBP (10% w/v in ethanol) into nitrocellulose propellant. (○) 40°C; (●) 50°C; (▲) 60°C; (■) 70°C.

illustrate. The times at which slope breaks occur agree well with the extrapolated times for complete penetration of the grain by the deterrent from the metrology.

The relationships between the fractional uptake of deterrents and time are given in Figures 4 to 6. Figures 7 to 9 show the relationships between depth of deterrent penetration and time.

The sorption of DBP and EC is clearly non-Fickian as the fractional uptake and penetration depth are both linear functions of time. This suggests a Case II diffusion mechanism consistent with the glassy state of the nitrocellulose and the swelling of the propellant grains which was observed. For ethanol/water solvents (*vide infra*) the swelling was large and resulted in cracking of the grain at longer time intervals. Further evidence for a swollen

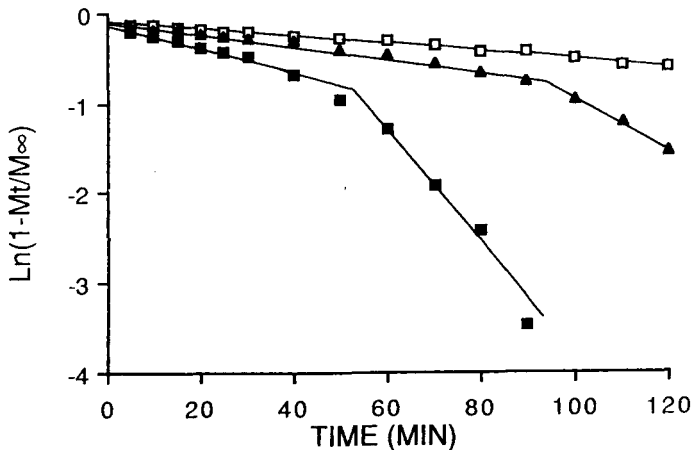


Fig. 2. Sorption of EC (10% w/v in ethanol) into nitrocellulose propellant. (□) 40°C; (▲) 50°C; (■) 60°C.

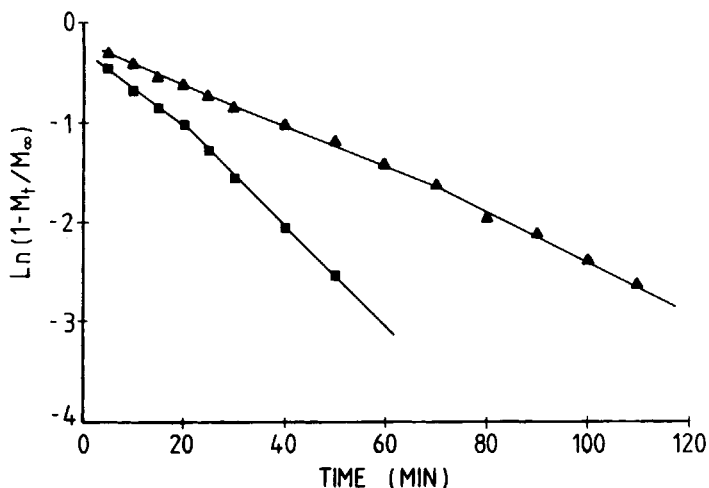


Fig. 3. Sorption of DNT (10% w/v in ethanol) into nitrocellulose propellant. (▲) 60°C; (■) 70°C.

gel layer was the tendency of the grains to stick together as the experiment progressed. It was clear that EC diffused more slowly into the matrix than DBP under all conditions. These results are consistent with those of Lewis¹⁸ and Campbell and Johnson,¹⁵ who found Case II diffusion behavior for sorption of acetone vapour and liquid in cellulose nitrate films.

The diffusion of DNT into the nitrocellulose matrix was Fickian, the fractional mass uptake varying as the square root time (Fig. 6). The depth of penetration exhibited a similar relationship with square root time (Fig. 9). Diffusion of DNT solutions into the matrix produced negligible swelling. Secondary indications of the formation of a swollen gel band on the outside of the grain, such as grains adhering to one another, were also absent for DNT.

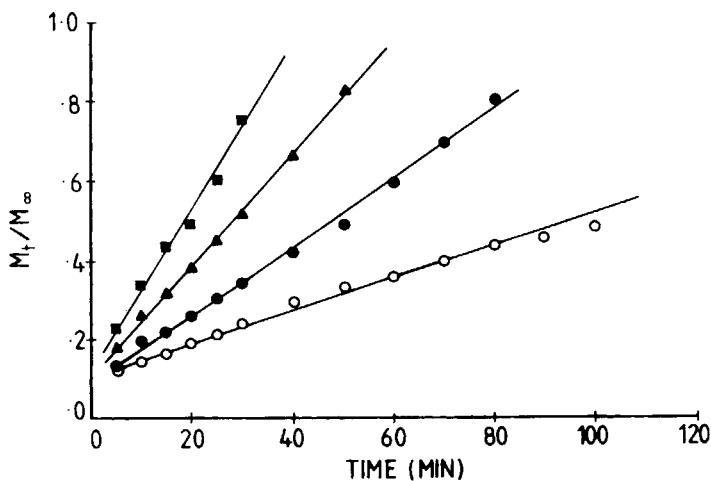


Fig. 4. Fractional mass uptake (M_t/M_∞) versus time for sorption of DBP (10% w/v in ethanol) into nitrocellulose propellant. (○) 40°C; (●) 50°C; (▲) 60°C; (■) 70°C.

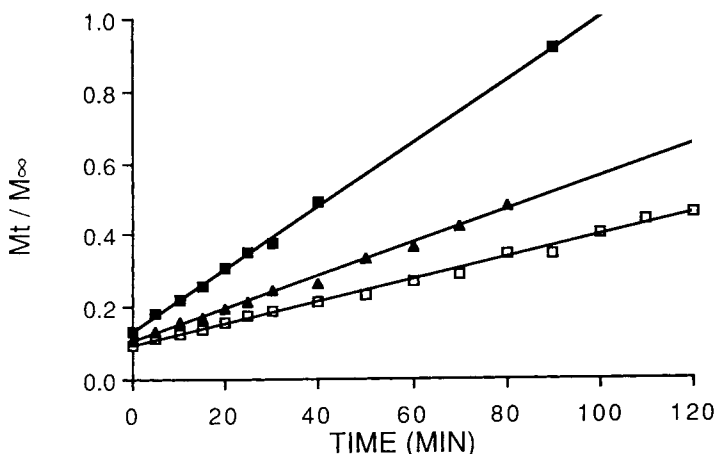


Fig. 5. Fractional mass uptake (M_t/M_∞) versus time for sorption of EC (10% w/v in ethanol) into nitrocellulose propellant. (□) 40°C; (▲) 50°C; (■) 60°C.

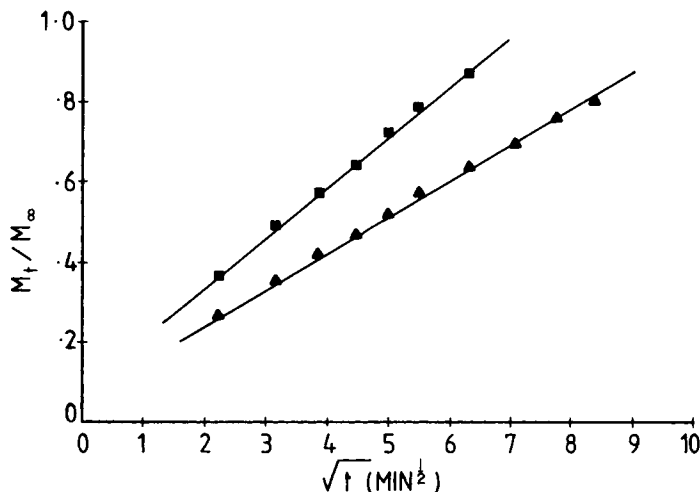


Fig. 6. Fractional mass uptake (M_t/M_∞) versus $\text{time}^{1/2}$ for sorption of DNT (10% w/v in ethanol) into nitrocellulose propellant. (▲) 60°C; (■) 70°C.

Unlike DBP and EC, DNT is unable to form strong hydrogen bonds to the nitrocellulose matrix. The degree of esterification of the cellulose is such that approximately one free hydroxyl remains per two pyranose rings on average (although regions inaccessible to nitration will exist in the matrix which will be totally unesterified). DNT is likely to interact less strongly with the NC matrix (mainly by a dipole-dipole interaction) and may not swell the matrix as much as DBP and EC which can form hydrogen bonds to it.

Effect of Temperature

As the preceding data clearly indicate, increasing temperature will increase both the rate of mass sorption and the velocity of the advancing front. It is possible to obtain an estimate of the apparent activation energy⁶ for Case II

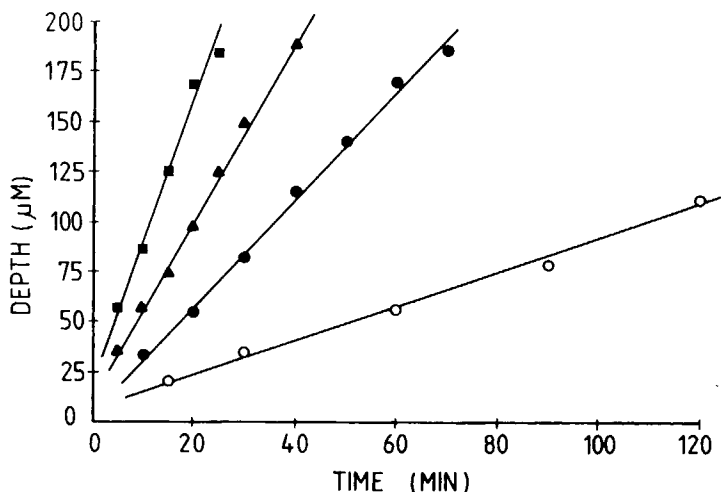


Fig. 7. Penetration rate of DBP (10% w/v in ethanol) into nitrocellulose propellant. (○) 40°C; (●) 50°C; (▲) 60°C; (■) 70°C.

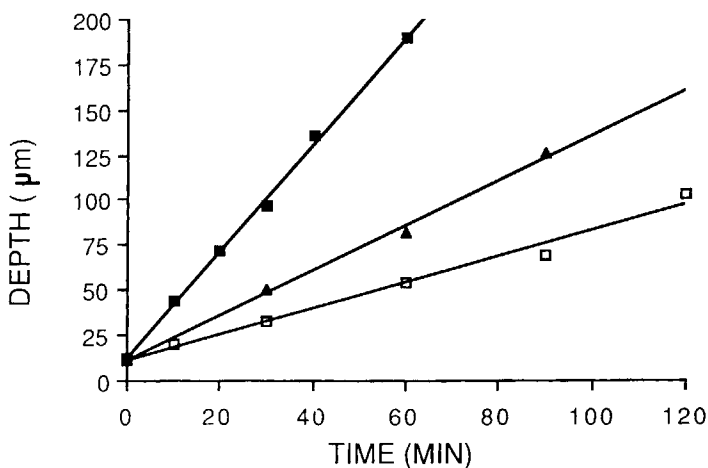


Fig. 8. Penetration rate of EC (10% w/v in ethanol) into nitrocellulose propellant. (□) 40°C; (▲) 50°C; (■) 60°C.

diffusion from an Arrhenius plot of the penetration data given in Figures 7 and 8. The Arrhenius plot (Fig. 10) yielded an activation energy of 62 kJ/mol for DBP diffusion and 66 kJ/mol for EC diffusion by least-squares fit. The difference in these values is not significant as it lies within the range of experimental error. These values are comparable with activation energies of 59 kJ/mol for diffusion of water in cellulose-filled polymers¹⁹ and 71 kJ/mol for creep of glassy PMMA.²⁰

2:1 Ethanol / Water Solvent

Increasing the polarity of the solvent in which the deterrents were dissolved by use of 2:1 v/v ethanol/water appeared to have no effect on the mecha-

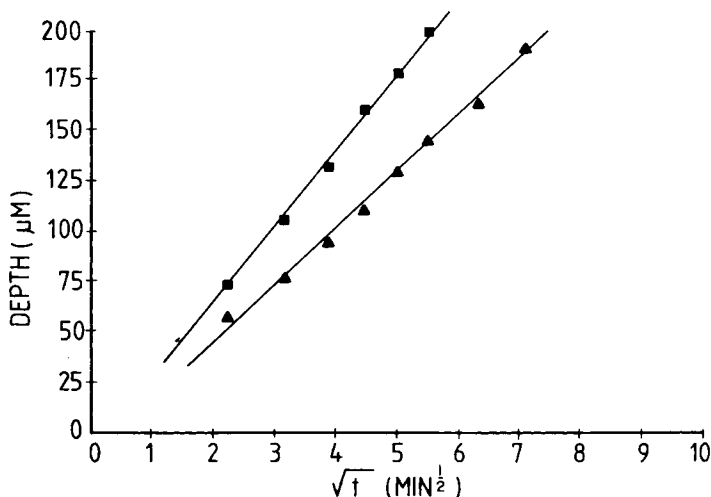


Fig. 9. Penetration rate of DNT (10% w/v in ethanol) into nitrocellulose propellant. (▲) 60°C; (■) 70°C.

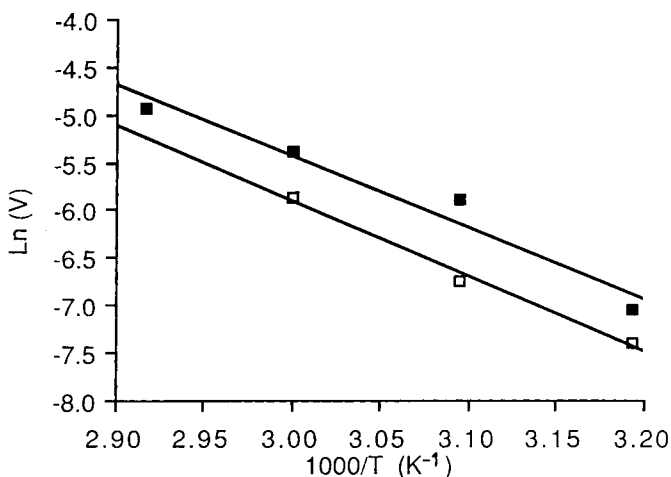


Fig. 10. Arrhenius plot of natural logarithm of penetration rate (mm/min) versus reciprocal temperature for (■) DBP and (□) EC (Case II) diffusion in nitrocellulose propellant.

nism of diffusion. DBP and EC again exhibited a linear relationship between fractional mass uptake M_t/M_∞ and time and between penetration depth and time (see Figs. 11–12). The formation of an outer, swollen gel layer was more marked with the polar solvent, with grain outer diameters increasing by as much as 10% for long contact times. There was increased evidence of stress fracturing in the glassy core with this solvent. The increase in solvent polarity markedly reduced the rate of penetration of EC into the grain but had little effect on the penetration of DBP. The rate of fractional mass uptake of EC and DBP into the grain was relatively unaffected by the solvent change.

The diffusion of an ethanol/water solution of DNT exhibited an essentially identical diffusion mechanism and rate as a neat ethanol solution, as Figures

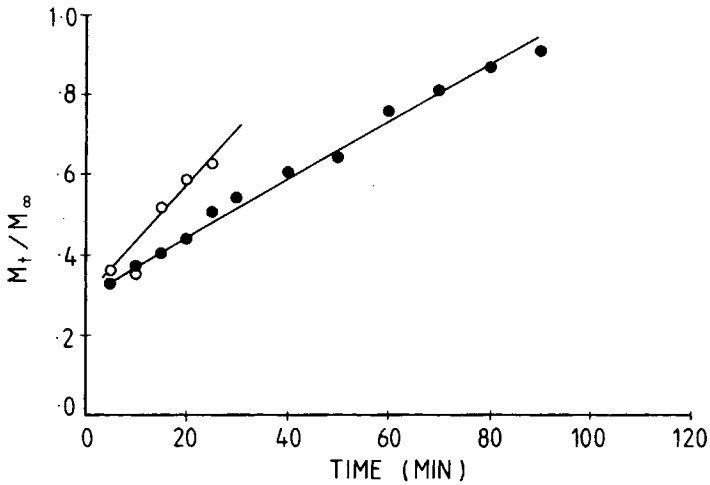


Fig. 11. Fractional mass uptake versus time for sorption of (○) DBP and (●) EC (10% w/v solutions in 2:1 v/v ethanol/water) into nitrocellulose propellant at 63°C.

13 and 14 indicate. A preliminary study of DNT diffusion in single-base propellant by Fong and Cooke¹⁶ showed that this is true for even a wider range of solvent polarities than considered here.

One purpose of investigating the interactions of deterrent solutions with "real" propellants is to gain control over the depth of the deterred layer in the grain and its deterrent concentration for ballistic optimization. This work has indicated that such control is possible by manipulation of coating time, solvent type, and temperature (and presumably the concentration of deterrent solution, which was not a variable here).

For a hollow cylinder outer radius b , inner radius a , with deterrent penetration depth $S(t)$ on the outer surface and $S(t)/2$ on the inner surface,

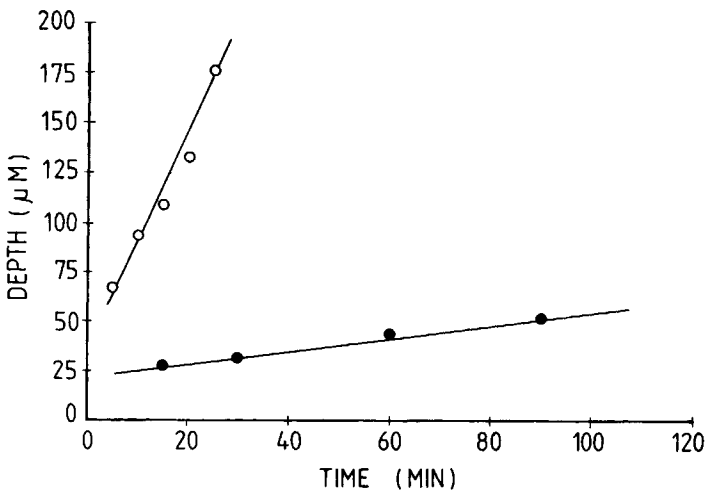


Fig. 12. Penetration rate of (○) DBP and (●) EC (10% w/v solutions in 2:1 v/v ethanol/water) into nitrocellulose propellant at 63°C.

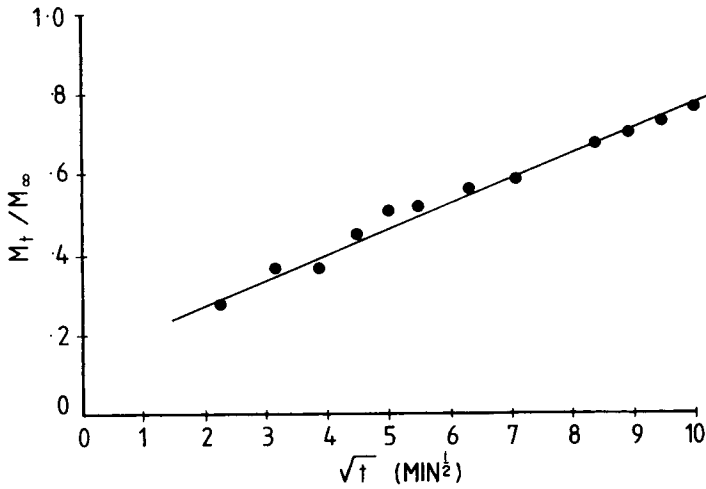


Fig. 13. Fractional mass uptake of DNT versus time^{1/2} (10% w/v solution in 2:1 v/v ethanol/water) into nitrocellulose propellant at 63°C.

the following relationship may be derived

$$P_d \approx (M/S(t)) (b^2 - a^2) / \left(2 \left(b + \frac{a}{2} \right) \right)$$

where P_d is the percentage of deterrent in the deterred bands and M is the percentage of deterrent in the whole propellant grain. Utilizing the grain dimensions for AR2206 this reduces to (for a Case II concentration profile)

$$P_d \approx 0.163 M/S$$

The percentage of deterrent in the whole grain and the deterrent penetration depth depend in the same way on time so that M/S is a constant at any given

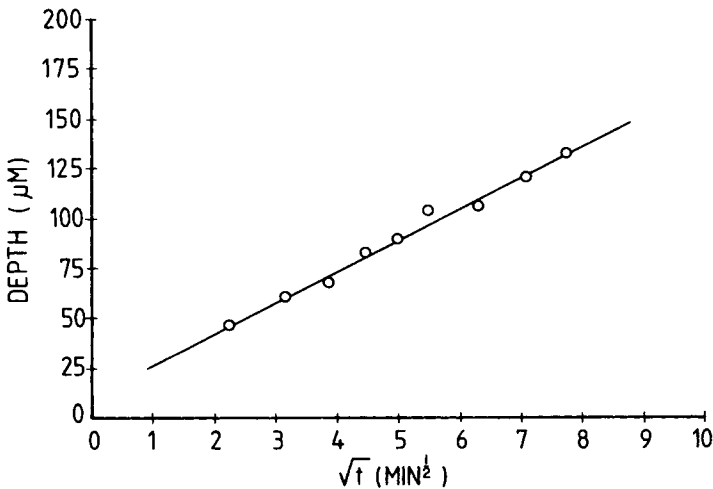


Fig. 14. Penetration rate of DNT (10% w/v solution in 2:1 v/v ethanol/water) into nitrocellulose propellant at 63°C.

temperature (as Case II diffusion implies). Consequently, by varying the coating temperature and coating time, the depth and concentration of the deterred bands in the propellant grain may be varied independently over a range of values. This range may be extended by using a solvent of different polarity. The above analysis assumes that the concentration of deterrent in the band is independent of radial distance. A similar relationship can be derived for Fickian radial concentration profiles. The activation energies for diffusion can similarly be used to predict the penetration data at temperatures other than those studied.

CONCLUSION

The diffusion of solutions of the deterrents EC and DBP into single-base (predominantly nitrocellulose) propellants can be described by a Case II diffusion mechanism which requires that the fraction of deterrent taken up and its depth of penetration be linear functions of time. The diffusion of DNT solutions is Fickian (Case I). The diffusion behavior of EC is sensitive to the polarity of the solvent. The concentration of deterrent in the deterred layer of the propellant and the thickness of the layer may be varied independently over a range of values to give the desired ballistic characteristics.

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