Diffusion of Deterrents into a Nitrocellulose Matrix. An Example of Diffusion with Interaction

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Synopsis

The diffusion of various concentrations of a deterrent (di-*n*-butyl phthalate) into a spherical, nitroglycerin-containing nitrocellulose matrix was studied. It was concluded that the final concentration profile could best be explained by a diffusion with interaction mechanism. Based on this mechanism, a method for calculating the depth of deterrent penetration is presented.

INTRODUCTION

Deterrents are materials which are diffused some distance into nitrocellulose-based, small-arms propellants in order to slow down their initial burning rate when the total grain surface area is at maximum. Small variations in the depth of penetration and concentration of deterrents in a small-arms propellant have been found to have a dramatic effect on the propellant's ballistic performance. For this reason, a study was made of the depth of penetration of di-*n*-butyl phthalate (DBP, a deterrent) obtained when various concentrations were diffused (utilizing a scaled-down production technique) into a spherical, double-base (nitroglycerin-containing) nitrocellulose matrix.

Past work to establish methods for measuring the depth of DBP penetration into a nitrocellulose (NC) matrix utilized staining[1,2] and optical techniques.[3] Levy[3] postulated a shallow deterrent gradient from the diffusion front to the grain surface and measured the effect of concentration and other process variables on depth of deterrent penetration. An autoradiographic study[4] of the DBP concentration profile in a spherical NC matrix showed that the concentration of DBP was level through the body of the deterred region (which is only a portion of the grain diameter), with an abrupt drop in concentration, and that the visually observed depth corresponded to the actual depth. Further, this work[4] indicated that a diffusion with interaction mechanism could account for this type of concentration profile. An infrared study[5] has demonstrated that hydrogen bonding occurs between the carbonyl group of DBP and the unesterified hydroxyl groups in NC and also measured the lengths of these interactions. Brodman[6] has shown that hydrogen bonding occurs between unesterified hydroxyl groups in NC, and again the bond lengths were measured. However, the strength of the NC–OH interactions in pure NC was weaker than the deterrent–NC hydroxyl interactions. Further, a subsequent study[7] considered the

hydrogen bonding characteristics of both ethyl acetate (EA) and nitroglycerine (NG) in a NC matrix. These results indicated that EA does hydrogen bond to the unesterified hydroxyl groups in NC and that the bond strength of this interaction is the same as that obtained for the DBP–NC interaction. Also, it was shown[7] that NG does not hydrogen bond to unesterified hydroxyl groups in NC.

Herzog[8] described the NG impregnation process and has shown by microscopic examination of sectioned grains that the residual EA which remains in propellant grains prior to deterring is concentrated at the surface of the grain. Further, this reference indicated that some residual solvent should be left in the grain in order to facilitate deterring.

EXPERIMENTAL

NC spheres used in this study were undeterred WC870 ball propellant made by Badger Army Ammunition Plant. The moisture-free composition of the NC spheres was 1.22% diphenylamine, 0.49% EA, 0.64% DNT, 0.31% DBP (both DNT and EA are present as contaminants), 9.40% NG, and 87.94% NC (13.15% N) determined by difference from a solvent extractable fraction. The spheres ranged in size from 0.034 to 0.027 in. Purified di-n-butyl phthalate was obtained from Fisher Scientific Co.

Scaled-Down Deterring Process. WC870 propellant, 200 g, 500 ml water and 1.3 g Swifts Colloid #1 (Swift and Co.) were placed in a 2-liter, three-neck flask equipped with a stirring blade and a condenser. During the deterring process, the flask was placed in a constant-temperature water bath and maintained at 76° ± 0.5°C. A separate emulsion of DBP was prepared by dissolving 0.1 g Swifts #1 Colloid in 50 ml water and adding the appropriate amount of DBP to the solution. The DBP emulsion was maintained at 76°C prior to addition to the flask containing the propellant. An appropriate quantity of this emulsion which contained 3 parts of DBP to 5 parts of water/colloid was added to the deterring flask. After addition of the DBP emulsion, the flask was maintained at 76° ± 0.5°C for 6 hr with constant stirring. These conditions have been shown to result in quantitative transfer of the deterrent to the propellant grains. At the end of the 6-hr period, the liquid was poured off and the propellant was washed with 1 liter of water. After washing, the deterred propellant was allowed to air dry overnight at ambient temperature. Further migration of deterrent during washing, drying, and storage did not present a problem since past work[4] has shown that hydrogen bonding to NC occurs.

Microtoming. Thirty individual grains of the deterred propellant from each run were mounted on $1/8$ in. ceramic rods with Titebond Glue (Franklin Glue Co.) and microtomed into sections about 22 μ thick. The sections were then permanently mounted on microscope slides with Permount (Fisher Scientific Co.).

Measuring. The mounted grain segments were measured using a Unitron TMS-1566 measuring microscope equipped with a 10× eyepiece and 10× objective lens. The maximum error in measuring the depth of penetration was ±5 μ.

Determination of DBP and EA. Both DBP and EA were determined on the deterred grains by extracting the propellant with a methanol/acetone mixture. The resulting liquid extract was then subjected to gas-chromatographic analysis.[9]

DISCUSSION

The purpose of this study was to measure the depth of DBP penetration in a spherical, NG-containing, NC propellant grain and to provide a means for predicting the depth of penetration. This method of prediction was based on a diffusion with interaction mechanism and therefore had to consider other factors which would alter the extent of deterrent interaction. Further, this description is offered as an interesting general example of a nonclassical concentration profile (one which does not obey Fick's law) obtained from a case of diffusion with interaction.

The hydroxyl group density of the NC is important in DBP depth considerations since an interaction has been shown to exist between the deterrent carbonyl group and the unesterified hydroxyl groups in NC. The relationship used to establish the number of hydroxyl groups per repeat unit (N_{-OH}) based on NC nitrogen content (X_N) is given below:

$$N_{-OH} = 3.0 - \frac{(162.15)\,(X_N)}{14.01 - (45)\,(X_N)}. \qquad (1)$$

The hydroxyl group density (ρ_{-OH}) of the single-base grain can be calculated from the specific gravity (ρ_{sb}) and the number of hydroxyl groups per NC repeat unit according to the following equation:

$$\rho_{-OH} = \frac{\rho_{sb}\,N_{-OH}}{W_{NC\,unit}}\,[1 - (X_{DPA} + X_{DBP_i} + X_{DNT})] \qquad (2)$$

where $W_{NC\,unit}$ is the gram-molecular weight of a NC repeat unit and X_{DPA}, X_{DNT}, and X_{DBP_i} are the weight fractions of diphenylamine, dinitrotoluene, and dibutylphthalate present as either stabilizer (DPA) or contaminants (DNT, DBP) in the single-base grain.

In similar fashion, the initial molecular densities of DBP and EA (ρ_{DBP_i}, ρ_{EA_i}) were calculated. Since the initial DBP content of the propellant is distributed homogeneously, the hydroxyl group density was corrected for the DBP–NC$_{-OH}$ interaction in the following way:

$$\rho_{OH}' = \rho_{-OH} - \rho_{DBP_i} \qquad (3)$$

where ρ_{-OH}' is the density of hydroxyl groups which are available for further interaction. Because of the complex nature of the NC matrix, a certain fraction of NC$_{-OH}$ groups would be precluded from an interaction. Therefore, it became necessary to correct ρ_{-OH}' for steric hindrance.

The hydroxyl group density that is available and accessible for interaction is given below:

$$\rho^{*}_{-OH} = \rho_{-OH}'\,(1 - X_{-OH\,hind}) \qquad (4)$$

where $X_{-OH\,hind}$ represents the fraction of sterically hindered hydroxyl groups.

Since the residual solvent (EA) has been shown to hydrogen bond through its carbonyl group with NC$_{-OH}$ groups and the resulting strength is the same as that for the DBP, NC$_{-OH}$ interaction, a number of NC$_{-OH}$ groups are blocked from DBP–NC interaction. Also, previous work has shown that due to manufacturing conditions, the EA is found near the surface of the grain. Consequently, in the development of the following prediction, the EA was treated
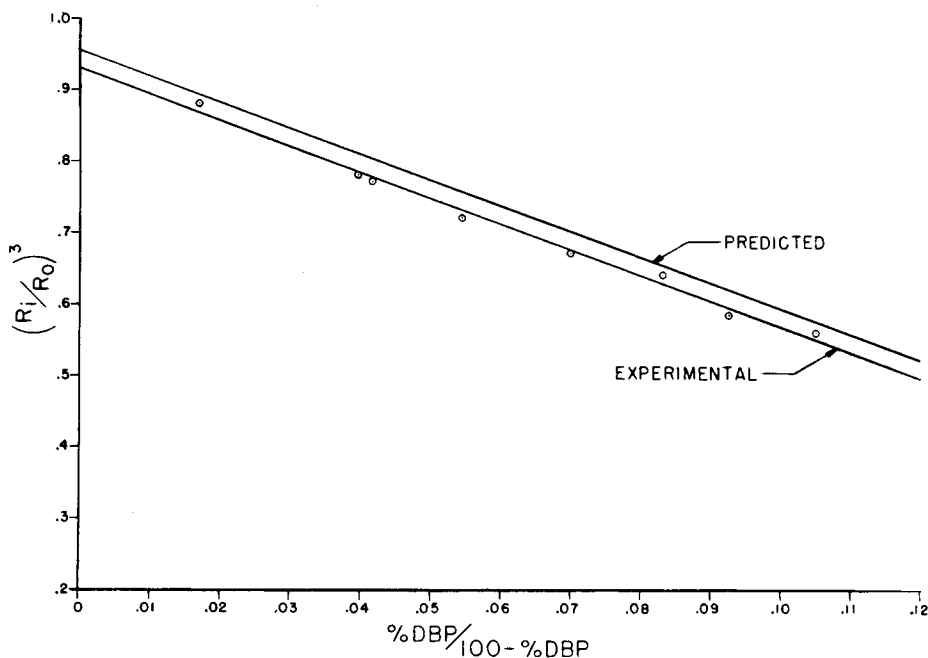
Fig. 1. Predicted and experimental values of $(R_i/R_0)^3$ for varying DBP concentration.

as a molecule of DBP and therefore distributed homogeneously throughout the deterred region. From geometric considerations, the following statement was formulated.

$$\frac{4}{3} \Pi R_i{}^3 = \frac{4}{3} \Pi R_0{}^3 - \left\{ \frac{4}{3} \frac{\Pi R_0{}^3}{\rho^*_{-OH}} \left[\frac{\rho_{db} N_{av}}{MW_{DBP}} \left(\frac{X_{DBP}}{1 - X_{DBP}} \right) - \rho_{DBP i} + \rho_{EA i} \right] \right\}. \quad (5)$$

The term in braces in eq. (5) reflects the volume of the deterred region based on the weight fraction of DBP (X_{DBP}) in the propellant and the available and accessible —OH group density. By collecting terms and simplifying, the following relationship was obtained:

$$(R_i/R_0)^3 = \left[1 + \frac{(\rho_{DBP i} - \rho_{EA i})}{\rho^*_{-OH}} \right] - \left[\frac{(\rho_{db})(N_{av})}{(MW_{DBP})(\rho^*_{-OH})} \right] \frac{X_{DBP}}{1 - X_{DBP}} \quad (6)$$

where ρ_{db} represents the double-base density (NG containing) of the propellant, N_{av} is Avogadro's number, and MW_{DBP} is the gram-molecular weight of DBP.

The depth of penetration is calculated as $(R_i/R_0)^3$ to avoid particle size variations. It was found that a 12.3% steric factor provided the best fit for the slope and that all other steric factors used in this calculation produced a line which was not parallel to the experimental line shown in Figure 1. The only variable which would affect the slope of the calculated line is ρ^*_{-OH}. Factors which could cause variation in ρ^*_{-OH} are degree of nitration, which was known and accounted for, and steric hindrance. Therefore, it was reasonable to include a steric hindrance factor in the calculation. Further, it seems likely that a certain fraction of the hydroxyl groups is hindered since it survived the nitration reaction. As can be seen in Figure 1, there is fairly good agreement between the calculated line and the experimental line. The experimental data were ob-

TABLE I
Comparison of Calculated and Experimental Depth Data

DBP, %	Calculated depth, μ[a]	Experimental depth, μ	Δ, μ
1.67	14.95	16.26	1
3.77	26.97	32.00	5
3.98	28.48	33.27	5
5.17	36.12	42.16	6
6.53	42.70	47.50	5
7.68	56.10	58.42	2
8.48	64.03	70.87	7
9.51	72.59	75.95	3

[a] Calculated from eq. (6) using the average propellant grain radius for each group.

tained by microtoming and measuring the diameter and depth of penetration of 30 grains at each concentration studied. In some cases, the grains were oblong so the major and minor axis were measured and the diameter taken as the average. DBP depths of penetration were calculated using eq. (6) and compared with the experimental results in Table I. As can be seen, the predicted depth was within experimental error of the measured depth in all but two cases.

These data indicated that the relationship between deterrent depth and concentration can best be described by a diffusion with interaction mechanism. Further, it has been shown that an interaction involving a second molecule, EA, can be used to alter the depth of penetration; and finally, a method for predicting the depth of deterrent penetration for a fixed time and temperature has been developed. Perhaps the more general lesson learned in this study is that a chemical interaction should be looked for when nonclassical concentration gradients are observed experimentally. Further, these interactions, in some cases, may be exploited in order to alter the depth of penetration, for a given concentration, by blocking interacting groups in the solid matrix. Finally, when interactions are responsible for nonclassical diffusion gradients, all factors which affect the interaction (such as steric hindrance) must be considered.

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