

# Benzoates as Deterrents for Small Arms Propellants

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## Synopsis

The depth of penetration of a homologous series of benzoic acid esters into a spherical nitrocellulose matrix was studied. It was found that the depth of penetration was related to the shift in infrared hydroxyl stretching frequency when the individual esters were incorporated into cast films of nitrocellulose. Further, these findings are discussed in terms of Taft's  $\sigma^*$  values for the individual esters. Conclusions regarding the use of benzoic acid esters as deterrents for small arms propellants were made.

## INTRODUCTION

Nitrocellulose (NC)-based small arms propellants utilize a material called a deterrent in order to moderate their burning rates early in the ballistic cycle when the surface area of the propellant is at maximum. In spherical-type propellant, di-*n*-butyl phthalate (DBP, a deterrent) is diffused into a portion of the propellant grain. The concentration profile of DBP in ball propellant was established by autoradiographic techniques.<sup>1</sup> This work indicated that the concentration of DBP was level throughout its depth of penetration with an abrupt drop-off at the boundary. Examination of sectioned grains under a microscope revealed the presence of a visually distinct concentric region around the periphery of the grain.<sup>1</sup> Measurement of the depth of this region and comparison with autoradiographic data indicated that it corresponded exactly to the visually observed deterred layer of the grain.<sup>1</sup> A series of subsequent studies established that hydrogen bonding occurs between a variety of deterrent materials<sup>2</sup> and unesterified hydroxyl groups in nitrocellulose. Specifically, the carbonyl groups of DBP hydrogen bond to the unesterified hydroxyl groups in nitrocellulose.

The depth of deterrent penetration into the nitrocellulose grain is an important parameter in charge design since it controls the gas generation schedule. This study describes a novel method for altering this depth for a given molar concentration of deterrent material, utilizing the information gained in the previous studies.<sup>1-4</sup>

## EXPERIMENTAL

Nitrocellulose spheres used in this study were undeterred WC 870 ball propellant made by Badger Army Ammunition Plant. The moisture-free composition of the NC spheres was 1.22% diphenylamine, 0.49% ethyl acetate (EA), 0.64% dinitrotoluene (DNT), 0.31% DBP (both DNT and DBP are present as

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contaminants), 9.40% nitroglycerine (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 0.27 in. (0.086 to 0.688 cm). The methyl benzoate was purchased from Aldrich Chemical Co., and the ethyl, propyl, and butyl benzoate were acquired from Eastman Organic Chemicals.

### Scaled-Down Detering Process

Two hundred grams of WC 870 propellant, 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 detering process the flask was placed in a constant-temperature water bath and maintained at  $76^{\circ} \pm 0.5^{\circ}\text{C}$  for 6 hr with constant stirring.

A separate emulsion of each benzoate was prepared by dissolving 0.1 g of Swifts #1 Colloid in 50 ml water and adding the weight of benzoate shown in Table I. This emulsion was maintained at  $76^{\circ}\text{C}$  prior to addition to the flask. The amount of deterrent suspension added to the flask is given in Table I. After addition of the deterrent emulsion, the flask was maintained at  $76^{\circ} \pm 0.5^{\circ}\text{C}$  for 6 hr with constant stirring. These conditions have been shown to result in the quantitative transfer of deterrent to the propellant grains.

At the end of the 6-hr period the liquid was poured off and the propellant washed with 1 liter water. After washing the deterred propellant was allowed to air dry overnight at ambient temperature.

### Microtoming

Thirty individual grains of the deterred propellant from each run were mounted on  $\frac{1}{8}$ -in. ceramic rods with Titebond Glue (Franklin Glue Co.) and microtomed into sections about  $22 \mu$  thick. The sections were then mounted on microscope slides with Permunt (Fisher Scientific Co.).

### Measuring

The mounted grain segments were examined using a Unitron TMS-1566 measuring microscope equipped with a  $10\times$  eyepiece and  $10\times$  objective lens. The maximum error in measuring the depth of penetration was  $\pm 5 \mu$ . The relative depth of penetration for each deterrent was determined by measuring the diameter and depth of penetration of the grains. In some cases the grains were oblong, so the major and minor axes were measured and the diameter taken as the average.

TABLE I  
Benzoate and Benzoate Emulsion Weights

Compound	Weight, g	Weight of emulsion, g
Methyl benzoate	5.87	9.78
Ethyl benzoate	6.47	10.79
<i>n</i> -Propyl benzoate	7.08	11.48
<i>n</i> -Butyl benzoate	7.68	12.80

TABLE II  
Taft Constants and Depth of Penetration Expressions

Compound	$\sigma^*$	$\left(\frac{R_i}{R_0}\right)^3$
Methyl benzoate	0.00	0.235
Ethyl benzoate	-0.10	0.255
<i>n</i> -Propyl benzoate	-0.12	0.350
<i>n</i> -Butyl benzoate	-0.13	0.480

### Discussion

The purpose of this study was to measure the depth of penetration of a homologous series of benzoic acid esters when diffused into a spherical nitroglycerine containing nitrocellulose propellant grain. Past work involving di-*n*-butyl phthalate has established that the concentration is level through the deterred region<sup>1</sup> and that hydrogen bonding occurred between the ester carbonyl group and the unesterified hydroxyl group in nitrocellulose.<sup>2</sup>

A subsequent study indicated that the observed concentration profile could best be explained by a diffusion with interaction mechanism.<sup>3</sup> In such a case, deterrent molecules would move into the nitrocellulose matrix until steric and electrostatic factors allowed an interaction to occur with unesterified hydroxyl groups in the nitrocellulose. Subsequent deterrent molecules would then be forced to move deeper into the grain in order to interact with these hydroxyl groups.

The benzoic acid esters are of potential interest as deterrent materials and for this reason were the subject of an investigation involving their hydrogen bonding properties when present in a nitrocellulose matrix. This study established that hydrogen bonding occurred between the benzoic acid ester carbonyl group and unesterified hydroxyl groups in nitrocellulose<sup>4</sup> and developed a relationship between Taft's  $\sigma^*$  value and the magnitude of the shift in the hydroxyl stretching frequency in the infrared.<sup>4</sup>

Methyl, ethyl, *n*-propyl, and *n*-butyl benzoate, at equivalent molar concentration, were diffused into ball propellant utilizing a scaled-down manufacturing technique. The resulting deterred propellant was microtomed, and both the diameter of the grain and the diameter of the undeterred region were measured. From these data the radius of the grain ( $R_0$ ) and the radius of the undeterred region ( $R_i$ ) were obtained.

In order to minimize the effect of particle size variation, the depth of penetration is expressed as  $(R_i/R_0)^3$ . These data for each benzoic acid ester are shown in Table II. It can be seen that the methyl ester gave the lowest value for  $(R_i/R_0)^3$ , indicating the deepest penetration into the grain. Figure 1 shows a correlation between  $(R_i/R_0)^3$  and the shifted hydroxyl stretching frequency data previously reported. There appears to be a linear relationship between depth of penetration and the observed shift in the hydroxyl stretching frequency.

Further examination of the Taft  $\sigma^*$  values (indication of the electron-donating effect of the various groups) listed in Table II shows that the molecule containing the group with the least electron-donating effect, the methyl group, penetrated deepest into the grain. As the Taft constants increase in magnitude, the electron donating effect of the group increases and more negative charge would be present

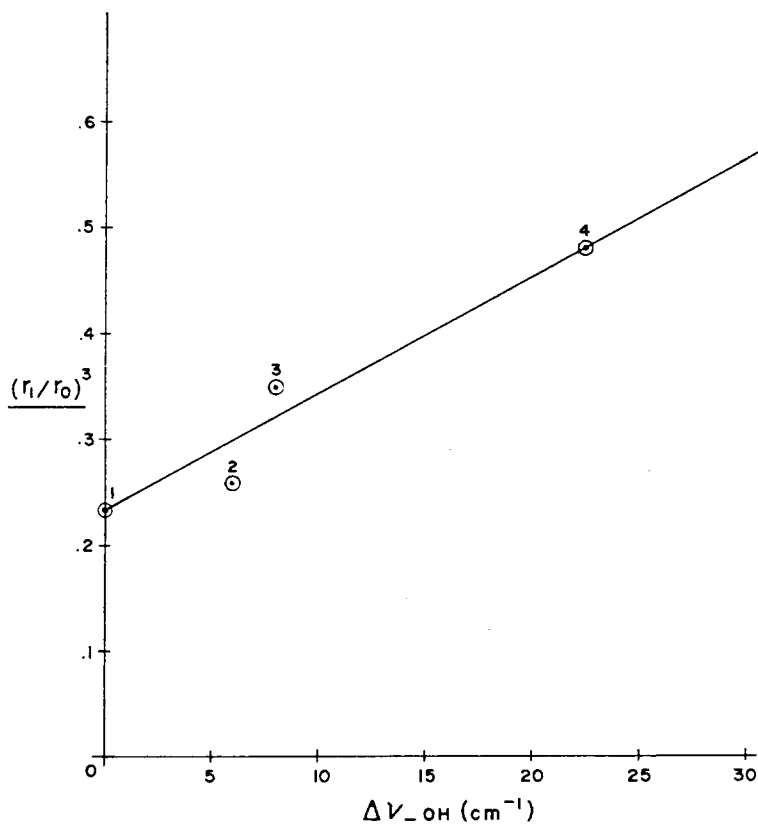
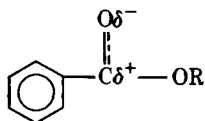


Fig. 1. Depth of penetration expression versus hydroxyl frequency shift.

on the carbonyl oxygen as shown below:



Thus, the methyl ester would have the least negative character, while the butyl ester would have the most. It appears that as a molecule is diffused into the nitrocellulose matrix, the likelihood of an interaction with a free hydroxyl group is enhanced by increased negative charge on the carbonyl oxygen. This explains why the methyl ester penetrated deepest into the grain while the butyl ester penetrated least. Thus, it appears that the depth of penetration of a deterrent can be regulated, for a given molar concentration, by the negative charge present on the carbonyl oxygen which in turn determines the likelihood of a hydrogen bond being formed. This finding could serve as a basis for evaluating potential deterrent materials as well as serving as a novel means for regulation of the propellant gas generation schedule.

### References

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