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Autoradiographic Determination of the Di-*n*-butyl Phthalate Concentration Profile in a Nitrocellulose Matrix

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Synopsis

The concentration profile of a deterrent (di-*n*-butyl phthalate) which had been diffused into a nitrocellulose sphere (ball propellant) containing nitroglycerin was studied by means of autoradiography. Results indicate a level concentration part way into the sphere with an abrupt dropoff in concentration. An explanation for this type of concentration profile is offered based on hydrogen bonding of the deterrent carbonyl group with unesterified hydroxyl groups in nitrocellulose.

INTRODUCTION

Deterrents are compounds which are diffused some distance into small-arms propellant grains to reduce their initial burning rate (when the propellant bed surface area is large). This reduction is accomplished by the endothermic decomposition of the deterrent. A knowledge of the concentration profile of deterrent in the propellant grain is important for manufacturing purposes as well as for prediction of ballistic performance. Several studies[1,2,3] have described methods for determining depth of deterrent penetration into small-arms propellant grains. However, these methods were not directly capable of measuring the concentration profile of deterrent in the grain. The first study[1] described a technique wherein a crystal violet dye is used to stain sectioned extruded propellant grains giving a purple color to the deterrent, permitting depth measurement.

A similar study[2] was made of nitroglycerin and dibutyl phthalate (DBP, a deterrent) penetration in ball propellant by using a visual boundary microscopically observed in sectioned ball propellant grains. By comparison with other studies dealing with diffusion of plasticizers into polymers, it was assumed that this observed optical boundary corresponded to a sharp concentration gradient associated with the DBP diffusion front. Also, it was inferred that a shallow plasticizer concentration gradient existed from the grain surface to the diffusion front.

A third study[3] in this area was concerned with correlation of DBP penetration depth with propellant burning rate. The penetration depth was

determined by using a crystal violet stain on grain segments, similar to the procedure described in reference 1. In the past, no direct measuring technique has been used to establish the concentration of DBP in the deterred region of the propellant grain. For this reason, a scaled-down production procedure was used to deter spherical nitrocellulose propellant grains (containing nitroglycerin) with ^{14}C-labeled DBP. Autoradiographs were then taken of the center section of these grains. The concentration profile of DBP in these spherical nitrocellulose grains was then determined from the autoradiographic data.

EXPERIMENTAL

Propellant. The ball propellant used for this study was WC 870, which was manufactured by Olin Corporation. It contained 10% impregnated nitroglycerin, and the size of the balls ranged from 0.0342 to 0.0257 in.

Deterring Process. Ball powder, 1.2 g, and 3.6 ml water were slurried in a test tube. The slurry was brought to 76°C in a constant-temperature bath and at the minimum stirring rate necessary to keep the ball powder suspended. Separately, an emulsion of DBP, Swift Colloid #1 (Swift & Co.), and water was prepared as follows: 0.1 g Swift Colloid #1 is added to 50 ml water and mixed until homogeneous; 1.00 ml was then mixed with 0.58 ml "cold" DBP and 0.020 ml tagged DBP (carboxyl 7-C-14, New England Nuclear, 1.00 millicurie). This mixture was brought to 76°C in the constant-temperature bath alongside the ball powder slurry. After vigorous agitation to uniformly distribute the DBP throughout the emulsion, an appropriate amount of emulsion was introduced into the ball powder slurry. The resulting mixture was then stirred at constant temperature. After 6 hr, the slurry was removed from the bath, the emulsion poured off, and the powder rinsed several times with a total of 40 ml water. The resulting deterred propellant was then air dried for a minimum of 72 hr at ambient temperature in a covered petri dish.

Microtoming. In preparation for microtoming the ball propellant, grains were mounted on a $^1/_8$-in.-diameter ceramic rod with a drop of Titebond glue manufactured by the Franklin Glue Co. (It had been determined that the glue contained no solvents which could alter the deterrent penetration characteristics.) The glue was allowed to set for 24 hr before sectioning.

A section thickness of 30 μ was found to be most suitable for the autoradiography. In order to obtain a section from near or at the center of the grain, the ball was microtomed until less than half remained, and the largest diameter section was taken to be the center section. To avoid contamination of the sample by the microtome blade, it was washed with $CHCl_3$ after using and shifted to a new position.

Autoradiography. The center segment of the deterred propellant grains was mounted on a microscope slide with a drop of Titebond glue. A transfer solution for the AR-10 (Kodak Ltd., London) film was prepared as

recommended by Kodak. Sucrose, 20 g, and 0.01 g potassium bromide were dissolved in 1 liter water. (This solution should be used immediately and prepared fresh on a daily basis.)

The slide with the mounted ball propellant segment was then covered with AR-10 film. A section of the film large enough to cover the specimen and overlap the edge of the slide was cut from the film plate. This film was then floated emulsion side down on the transfer solution such that the specimen was in contact with the photographic emulsion. The slide was then air dried at ambient temperature and stored during the exposure period (144 hr) in a light-tight box at 4°C.

After exposure, the AR-10 film was developed with gentle agitation for 5 min in D-19 developer (Kodak), washed in water for 1 min, and fixed in Acid Fixer (Kodak) for 6 min. After washing in water for 20 min, the film was transferred to a clean slide.

Photomicrography. Ball propellant segments were photographed utilizing bright field conditions through a Leitz Wetzlar Ortholux microscope equipped with a 5× eyepiece and 4× objectives lens. The camera used was a Nikon F2 with adapter and was loaded with Plus X-Pan film (Kodak-ASA 125). Exposures of $^1/_4$ sec were used.

Autoradiographs were photomicrographed using dark-field conditions with a 10× objective and a 5× eyepiece utilizing the previously described Nikon system. Exposures of 10 sec were used. The effective magnification obtained from the 10× objective was 32×.

In all cases, the Plus X-Pan film was developed for 8 min in a 1:1 water dilution of DK-50 developer (Kodak). Films were washed in water for 1 min, fixed for 6 min in Acid Fixer, and washed in running water for 20 min. The resulting negatives were air dried overnight.

Densitometry. The photomicrographs of the autoradiographs taken with the 10× objective were found to give images suitable for scanning on the Applied Research Laboratories Recording Densitometer. The densitometer output is a strip chart giving relative optical density. Each "densitometer unit" from the strip chart recording represents 4.34 μ on the autoradiographs taken with the 10× objective. The optical density measurements obtained from the densitometer scans were then converted to absorbance by running a series of standard filters on the densitometer and calibrated Perkin-Elmer Model 323 UV-VIS spectrophotometer. Relative transmittance was thus converted to absolute transmittance and then to absorbance using

$$\text{Absorbance} = -\log (\text{transmittance}).$$

The absorbance was then plotted versus "densitometer units" to illustrate the concentration gradient of DBP along a radius of the propellant grain.

ERROR DISCUSSION

There were several potential error sources which include β-scattering and self-absorption. These will be discussed individually.

β-Scattering. With the AR-10 emulsion (used in this study), more than 96% of the exposed silver grains will be contained within 5 μ of the source. This gives a resolution of about 10 μ on the autoradiograph and is the largest source of error involved in this investigation.

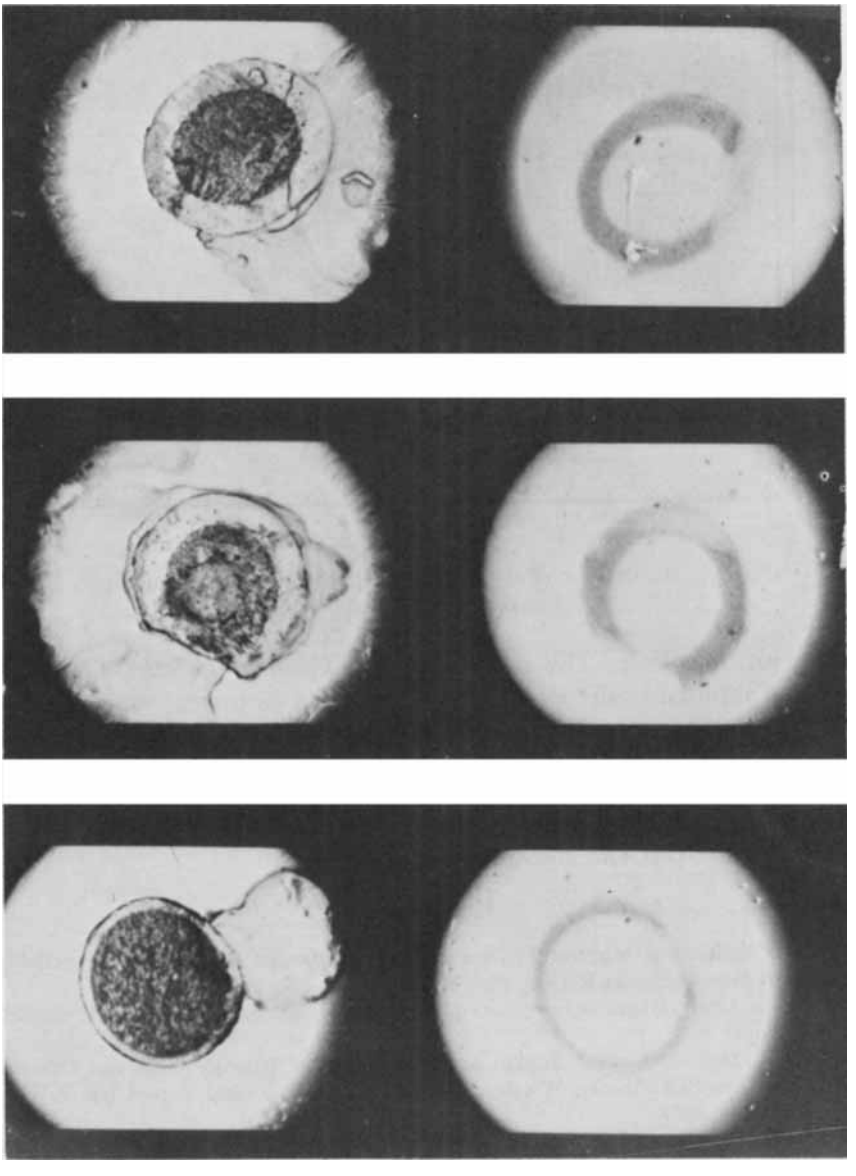
Self-Absorption. It has been found that some β-particles will penetrate up to 30 μ of nitrocellulose and still be capable of exposing the photographic emulsion. This indicates that β-particles will not be completely absorbed by the surrounding nitrocellulose and will lead to exposure of the film outside the area actually containing DBP. This condition leads to difficulty in defining the inner boundary of DBP penetration.

Film Configuration. The AR-10 film may drape itself over the samples in several ways. One of those configurations creates a boundary line in the developed autoradiograph at the segment's outer edge. Other configurations did not allow such exact determination of the outer edge of the segment. Fortunately, the most predominant configuration encountered is the former which allowed relatively clear definition of the outer segment edge on the autoradiographs.

Film Shrinkage. AR-10 film was found to shrink about 10% generally and occasionally as much as 15%, though this much shrinkage was rare. It was found that the film shrinkage did not affect the results of this study.

RESULTS AND DISCUSSION

^{14}C-labeled DBP was diffused into nitrocellulose spheres utilizing a scaled-down production technique. The resulting deterred propellant grains were microtomed, and the center sections were placed in contact with a photographic emulsion. Resulting autoradiographs were photographed through a microscope, and DBP concentration profile data was obtained by scanning the autoradiographs with a densitometer. Figure 1 shows typical autoradiographs of a deterred nitrocellulose grain along with their optical images. Figure 2 shows a composite representation of data obtained for 80 grains after 144 hr of exposing the grains to the photographic emulsion. It appears that there is a level concentration of deterrent through a region of the propellant grain with an abrupt drop in concentration. Further, it can be seen that the depth of deterrent penetration observed visually directly corresponds to that observed on the autoradiograph. It is interesting that the observed concentration profile does not correspond to a classical diffusion case which would initially predict an exponential concentration decrease from the surface inward that would, with time, tend to become level and penetrate through the entire grain. Several recent studies[4,5] have dealt with the hydrogen bonding of deterrents to unesterified hydroxyl groups in nitrocellulose and hydrogen bonding between OH groups in nitrocellulose. It has been shown that DBP does hydrogen bond to unesterified hydroxyl groups in nitrocellulose and that this interaction is stronger than the hydroxyl nitrocellulose interaction. Based on the results obtained in this study, coupled with the hydrogen



Section Autoradiograph

Fig. 1. Photomicrographs of ball propellant segments containing labeled di-*n*-butyl phthalate and corresponding autoradiographs.

bonding information, it appears that deterrent penetration into a propellant matrix is best described by a diffusion with interaction mechanism. In such a mechanism, DBP moves into the propellant grain by diffusion, and molecules are removed from the diffusion stream by hydrogen bonding between the carbonyl group of the deterrent and unesterified hydroxyl groups

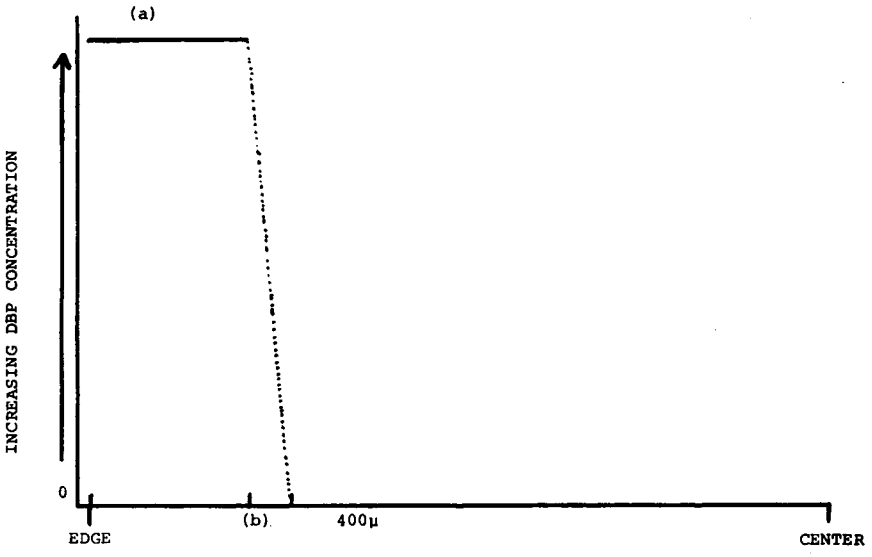


Fig. 2. Concentration of di-*n*-butyl phthalate as a function of distance into a nitrocellulose sphere.

in the nitrocellulose. This mechanism would lead to the level concentration and abrupt drop in concentration observed in the present study.

Further, it appears that the deterrent carbonyl–nitrocellulose hydroxyl interaction is sufficiently strong to prevent leveling of the concentration throughout the grain at ambient or slightly higher temperatures. However, DBP migration has been noted in nitrocellulose–nitroglycerin systems exposed to extreme storage temperatures.

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