An Example of the Effect of Chemical Interactions on Transport Phenomena

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Chemical interactions frequently affect transport processes and if these interactions are fully understood they can be exploited in order to obtain novel effects. The purpose of presenting these results is to demonstrate how these interactions can be used to alter the transport process, and in so doing, obtain a superior product. The specific process studied was the deterring of small arms propellants.

Deterrents are compounds which are diffused into spherical nitrocellulose based small arms propellant grains to slow down their initial burning rate. These deterrents are diffused part way into the grain, such that the burning rate reduction is present only when the propellant surface area is large. It has been found that a specific depth of deterrent penetration and nominal deterrent concentration is needed in order to meet ballistic specifications.

A recent study (Brodman et al., 1974a) has shown that hydrogen bonding occurs between certain deterrent molecules and unesterified hydroxyl groups in nitrocellulose, and the bond strengths for these interactions have been measured. Hydrogen bonding in nitrocellulose has also been studied (Brodman et al., 1974b), and it was concluded that weak hydrogen bonds were formed, involving only the nitrocellulose hydroxyl groups. Based on this information it seems likely that during production deterrent molecules move into the propellant grain by diffusion and interact with the first readily available unesterified hydroxyl group.

The molecules then remain bonded to this site, thus being removed from the diffusion current. Subsequent deterrent molecules would then move further into the grain and interact in a similar manner. Therefore, a consideration of the hydrogen bonding characteristics of other materials which are present in the grain at the time of deterring is important in controlling deterrent depth and concentration profile.

In the process used at Badger Army Ammunition Plant (to make ball propellant) the grain is treated with a solution of nitroglycerine in ethyl acetate and then the bulk of the ethyl acetate is distilled prior to the deterring step (Maag, 1962). Some ethyl acetate is intentionally left in the grain because it has been determined through experience that it is necessary to obtain the required depth of deterrent penetration (Herzog, 1946). The purpose of the present experimental work is to determine the hydrogen bonding characteristics of ethyl acetate and nitroglycerine, and to relate these findings to transport phenomena involved in the process.

EXPERIMENT

Infrared spectra were run of a cast film of nitrocellulose (nitrogen content 12.63%) containing a small amount of MC&B reagent grade ethyl acetate.

IR data for the nitrocellulose-nitroglycerine systems were obtained by dissolving ball propellant grains (containing nitrocellulose and nitrogycerine along with some trace inorganics, nitrocellulose nitrogen content 13.05 to 13.20% nitrogen). Cast films resulting from these solutions were run for each of the samples shown in Table 1.

IR data for the corresponding nitrocellulose samples alone was obtained by extracting each propellant sample with Fisher Certified ACS Grade Methylene Chloride in a Soxhlet for 18 hrs. at 90°C. This resulted in the removal of the nitroglycerine. All infrared data was obtained using a Perkin Elmer infrared spectrophotometer model number 621 under dry air purge conditions and with a 5X-abscissa expansion. The ν-OH ranges for each sample reported in Table 1 represent a minimum of five runs.

RESULTS

The hydrogen bonding characteristics of nitroglycerine and ethyl acetate with unesterified hydroxyl groups in nitrocellulose were studied by means of infrared spectroscopy. The ν-OH for a specific nitrocellulose sample was determined in a cast film with and without ethyl acetate present. With ethyl acetate present the ν-OH was measured at 3480 cm^{-1} indicating a small shift from the ν-OH (3500 cm^{-1}) measured with no ethyl acetate present. It should be noted that the nitrocellulose ν-OH with ethyl acetate present is exactly the same as that obtained for di-*n*-butyl phthalate in a similar nitrocellulose cast film (Brodman et al., 1974a). Di-*n*-butyl phthalate is the specific deterrent used in the ball propellant deterring process described in the introduction. It therefore appears that ethyl acetate does hydrogen bond to unesterified hydroxyl groups in nitrocellulose and that the bond strength for the nitrocellulose-ethyl acetate interaction is the same as that for the nitrocellulose deterrent interaction.

Studies of the hydrogen bonding characteristics of nitroglycerine with unesterified hydroxyl groups in nitrocellulose were performed by measuring the ν-OH of actual propellant grains which had been dissolved in ethyl acetate and cast as films on salt plates. By dissolving the total propellant grains containing only nitrocellulose, nitroglycerine, and trace inorganics, in this way samples of nitrocellulose with varying nitroglycerine contents were obtained. Table 1 shows the nitroglycerine content for the three samples used together with the infrared data. The ν-OH for each of the three samples were then measured as cast films resulting from propellant grains extracted with methylene chloride. This extraction totally removed the nitroglycerine which was present in the propellant grain. By performing the experiment in this way the ν-OH was measured for nitrocellulose-nitroglycerine samples with 10, 20.3, and

TABLE 1. SAMPLES

Sample	Nitroglycerine, %	ν-OH (cm^{-1}) before extraction	ν-OH (cm^{-1}) after extraction
1	10.00	3554-56	3552-54
2	20.30	3548-50	3548-50
3	28.84	3540-43	3536-40

All spectra were run with a dry air purge and a 5X expansion of the abscissa. The range of values indicates the variation obtained from a minimum of five runs for each sample.

28.84% nitroglycerine without having to handle nitroglycerine directly. It can be seen from Table 1 that the ν-OH obtained for a given nitrocellulose sample was essentially the same as for the corresponding nitroglycerine-nitrocellulose mixture. This then indicates that the nitroglycerine does not hydrogen bond with the hydroxyl groups present in nitrocellulose. This finding supports a similar conclusion drawn in a previous study (Brodman et al., 1974b) concerning hydrogen bonding of nitrocellulose nitrate ester groups to hydroxyl groups.

It should be pointed out that the ν-OH of nitrocellulose has been found to vary from specific sample to sample depending in part on the nitrogen content and molecular weight (Brodman et al., 1974b). This effect can be observed in the present data since each nitrocellulose sample has a different ν-OH. However, essentially the same ν-OH was obtained when nitroglycerine was present.

Implications of these findings on the small arms deterring process will now be discussed. The fact that ethyl acetate hydrogen bonds to unesterified hydroxyl groups in nitrocellulose and that the bond strength for this interaction is the same as that for the di-*n*-butyl phthalate-nitrocellulose interaction is significant in terms of the deterring process. This indicates that residual solvent in the grain can cause the deterrent to move in deeper by blocking available hydroxyl groups. Nitroglycerine does not hydrogen bond to nitrocellulose and therefore should not affect deterrent depth of penetration by bonding to unesterified hydroxyl groups.

Thus it can be seen that, for a given set of process conditions (time, temperature, and quantity), the transport phenomena can be altered through exploitation of the interactions involved.

LITERATURE CITED

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Manuscript received February 26, 1974; revision received March 26 and accepted April 12, 1974.

Entry Region for Steady Viscous Flow in Coiled Circular Pipes

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Coiled circular pipes are widely used in fluid flow, heat transfer, mass transfer, and chemical reaction applications. Consequently, a number of experimental and analytical studies concerning curved-tube transport phenomena have been reported as summarized by Austin (1971) and Kalb (1973). The viscous flow region has been of particular interest because of the significant departure of the transport coefficients from the values for straight pipe flow. However, almost all of the reported work has dealt with the case of steady state, fully developed flow.

In some applications, only partial or single coils may be used or the entry region of a multiple coil pipe may be critical; therefore, it is of interest to inquire into the nature of the flow in the entry region and the distance or degrees around the coil required to achieve essentially fully developed flow.

Keulegan and Beij (1937) collected pressure drop data on tubes of approximately 0.95 cm. I.D. for very gradual bends. Data were taken at points along the length of the coil in order to determine when the curved-tube pressure drop ceased to change with distance. They were able to predict an entrance length only under the assumption that it was not a function of the Reynolds number. Under this assumption, they were able to produce an empirical correlation for the entrance length as a function of the curvature ratio only. The purpose of this note is to present the results of a more detailed experimental study of the entry region under steady viscous flow conditions.

EXPERIMENTAL APPARATUS

The experiments were conducted with air flowing through coiled pipes constructed by Ilco Tubebending, Inc. from 4.445-cm. I.D. stainless steel pipe of 0.3175-cm. wall thickness. Pipes of four different curvature ratios (ratio of coil diameter to tube inside diameter) were used, namely 6.94, 9.06, 14.4, and 24.1. Each pipe had at least one complete coil turn. The air flow was first directed through a long straight pipe in order to establish a parabolic velocity profile before entering the coil. Coil pitch (ratio of distance between successive coil turns to

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