Sorption of Diethyl Phthalate by Nitrocellulose Fibers

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Synopsis

The manner in which diethyl phthalate (DEP) is absorbed into nitrocellulose (NC) fibers has been observed microscopically. The movement of pure DEP into dry fibers proceeds by capillary motion up the central canal (lumen) and through microcracks between fibrils. Attack, measured by a large change in birefringence, spreads from these foci, and within the time scale of the experiment there is little interaction with the primary (outer) wall of the fiber. If, however, the lumen and other capillary passages are blocked by water or other liquid, then attack proceeds evenly from the outer wall and a sharp boundary between swollen and unswollen material moves at a uniform speed towards the center of the fiber and appears to be unaffected by the fibrillar structure (Case II swelling). If the supply of DEP to the surface is interrupted, this boundary becomes immobile, and the concentration of DEP in the swollen layer is that which is just sufficient to saturate residual un-nitrated hydroxyl groups on the NC. Reducing the activity of the DEP by admixture with benzene results in similar sharp boundaries, presumably because capillaries become blocked with spent diluent. Apart from capillary action, movement is always perpendicular to the fiber axis.

INTRODUCTION

The kinetics of the sorption of vapors into nitrocellulose fibers and films have been extensively studied. Typical vapors have been acetone,[1,2] isopropyl nitrate,[2] and water.[2,3] Although the diffusion of water vapor is Fickian, both acetone and isopropyl nitrate give sharp boundaries moving linearly with time. Such behavior is typical of movement into glassy polymers and is generally referred to as "Case II swelling." The experimental difficulties involved in the study of sorption from liquids are much greater than those from the vapor.[4] For this reason sorption has been comparatively neglected, although optical microscopy has been used to study the surfaces of polymers during solution[4] and the sorption of dyes from solvent baths.[5] This neglect does not imply a lack of interest or importance, and the movement of liquid plasticizers into polymers is a field which deserves much greater attention. In this semiquantitative microscopic study diethyl phthalate (DEP) was chosen for a number of reasons. First, it is an important plasticizer for nitrocellulose (NC) (and other cellulosic materials) in the propellant industry. Second, its refractive index is close to that of NC which makes it a good immersion medium and allows detail to be seen without diffraction effects. Third, and most important, aromatic liquids, when absorbed into NC, cause very large changes in birefringence.[6] By measuring these birefringence changes by a suitable compensation technique an estimate of phthalate concentration may be obtained for any area which is large enough to be resolved in the microscopic field. The quantitative limitation of the method when applied to a fiber such as NC is due entirely to the indeterminate thickness of the specimen in the direction of the light path.

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EXPERIMENTAL

Two commercial samples of NC were used in this work. One sample, which contained 12.9% nitrogen, had been made at NEC Limited by the action of mixed nitric/sulfuric acid on cotton linters, and the other, which contained 12.4% nitrogen, had been made at the Royal Ordnance Factory, Bishopton, by the action of mixed acid on wood pulp. Both samples had undergone the normal commercial step of beating, which not only shortens the fibers, but leaves many regions in a damaged condition.

The DEP was a commercial sample supplied by Boake and Allen.

The optical compensation techniques used in this work have recently been described.[6] The de Senarmont method was found to be the most rapid and convenient and was used on the majority of occasions. Further notes on specimen preparation are given in later sections.

RESULTS AND DISCUSSION

Sorption of DEP into Dry Fibers

In these simple experiments a small sample of dry NC (12.9% N) was placed on a slide and covered with a thin glass slip. A drop of DEP was applied to the edge of the slip. Capillary action rapidly carried the DEP across the slide, and the effect on the NC fibers was observed under crossed polars.

Visually there appeared to be two distinct modes of interaction. In the first of these the fiber changed within about 5 s from the normal blue interference color to a mottled orange. The compensator showed a change from negative to positive birefringence. This mode of attack was generally apparent on those fibers which showed noticeable surface striations or damage of any sort. Here the outer wall was offering no protection, and since the sorption of DEP was far too fast to be explained by a diffusion process (either Fickian or Case II), movement was obviously by capillary action from the surface inwards. The fibers swelled rapidly to at least twice their original width, and surface striations were accentuated. The outlines then became indistinct, and were surrounded by much gelations material. Within 10 min no trace of the original fibers remained. This type of behavior could be seen both on complete fibers and on limited fiber lengths.

The second mode of attack occurred in those fibers which were of smooth appearance with few visible surface markings. Here the primary wall offered complete protection within the time scale of the observations (in some cases up to 30 min). The initial attack on such fibers was capillary movement up the lumen. A bright orange line appeared up the center of the fibers, generally within 5 s of contact with the DEP, but sometimes, in cases where the lumen was blocked, only after 10 or 15 min. Over a period of 10 min this central line expanded outwards until only thin slivers of unchanged NC remained. There appeared to be no attack on the outer wall, and no swelling of the fibers was observed until the last stages of sorption, when catastrophic breakdown occurred and the fibers swelled to over twice their original width. However, such fibers never dissolved completely, even after several days, indicating that they had greater overall structural integrity than those which were attacked by the first mechanism.

Thus the resistance of the NC structure towards sorption by DEP falls into three clear categories:

(a) The most resistant regions consist of *some* of the outer walls, which are basically unaffected and break up only under the pressure of the swollen material inside the fiber.

(b) Regions of fiber into which DEP passes with a sharp moving boundary. (Attempts to establish whether this movement followed a time or a root time law were inconclusive, and it cannot be said with certainty that a Case II mechanism is involved.)

(c) Regions where sorption is so rapid that quantitative conclusions cannot be reached from the present experiments. Capillary action along microcracks or fibril boundaries carried DEP rapidly throughout the region. The path length for any other diffusion mechanism is thereby greatly lowered and the whole region saturates within seconds.

It is interesting to note that those fibers having a resistant outer wall also showed an absence of microcracks since diffusion from the lumen always proceeded by means of a clear boundary, i.e., regions (a) and (c) were not present together along with any single length of fiber.

Sorption of DEP from a Water Slurry

When an experiment similar to that described above was carried out on NC fibers containing 30% w/w of water the capillary action was greatly retarded. Attack was on the lumen, but was delayed for several minutes. There was rarely evidence of rapid attack through microcracks, the first mechanism described in the previous section. It is important to understand the nature of the sorption of DEP by NC fibers in the presence of a large excess of water since this is the way in which plasticizers (including nitroglycerine) are normally added in the propellants industry. Refractive index differences make the direct observation of fibers immersed in water unsatisfactory, and the following procedure was adopted.

Weighed amounts of NC fibers were added to about 50 times their weight of water, and a slurry made by vigorous stirring. A weighed amount of DEP (in the form of a water emulsion) was slowly added. After mixing for 2 h the NC/DEP "paste" (a technical term in the propellant industry for swollen NC fibers) was filtered and dried under vacuum. The range of pastes prepared contained from 20 to 55% w/w of DEP. These dried pastes were then examined microscopically using Cargille oil immersion.

In the pastes containing 50% DEP and above, sorption was uniform throughout each fiber and all fibers were affected. In other words, no blue, optically negative, regions were apparent, but all fibers showed yellow, optically positive, birefringence. At DEP concentrations below 50% some fibers showed a similar total change, but as the DEP concentration fell an increasing number showed only partial conversion. In every case it was the outside of the fiber which had absorbed the DEP and a sharp boundary was visible between the outer, yellow region and the inner, blue region (this is, of course, the opposite effect from the lumen sorption described in the previous section where the outside is blue and the inside yellow). The most remarkable property of this boundary between swollen and unswollen fiber was its immobility. No change in position was ob-

served over a period of three months. Surprisingly little appears to be recorded in the literature on such immobile layers, although one would expect them to be a normal consequence of diffusion with reaction.

In the well-known process of deterrence of small-arms propellants, phthalates or other materials are diffused into the surface of what are mainly amorphous nitrocellulose grains. Here boundaries are known to be sharp and are presumed to be immobile.[7] Another recorded instance is in the transport of methanol into poly(methyl methacrylate).[8] Here microtomed sections were aged at 20°C for up to four days, and while emphasis was placed on the differences in concentration profile which *did* occur during this period, the position of the observed boundary changed less than might have been expected.

The boundary immobility suggested some form of chemical interaction which renders the DEP incapable of further movement. A measure of the critical DEP concentration which reacts is desirable in order to relate this stoichiometrically to some group on the NC molecule. It must be remembered that the distribution of DEP between fibers is not uniform. Some fibers will have more than the average amount added and some less. The procedure adopted was as follows. The path differences for 60 randomly selected fibers which had been uniformly swollen by the DEP (i.e., showed no boundaries) were measured by the de Senarmont compensator for each paste concentration. The path difference is shown in Figure 1. It should be noted that the line contains two slopes. The upper line represents those conditions under which all fibers in the sample are changed and the mean is a true representation of the average DEP concentration of the system. The lower line with steeper slope was taken under conditions where only some of the fibers were fully converted and hence measured. These fibers must contain more than their fair share of DEP and will have abnormally high birefringences. (No attempt was made to take measurements on partially converted fibers owing to the difficulty of estimating the thickness of the measured portion in the light path.) As the overall DEP concentration in the paste is diminished, fewer and fewer fibers will fulfill the conditions for measurement, i.e., total conversion, and those which do are likely to approach the critical DEP concentration required to bring about this conversion (see Fig. 2). Thus the extrapolated value for path difference at a DEP concentration of zero is taken as that which corresponds to the minimum DEP concentration which will open out the NC lattice. This minimum path difference is 12.5 nm, and corresponds with the edge of the observed histograms (Fig. 3).

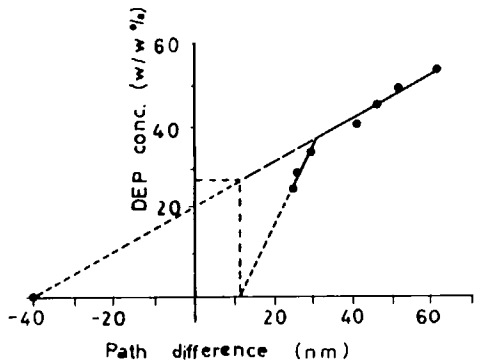

Fig. 1. Birefringence of DEP/NC (12.9% N) mixtures.

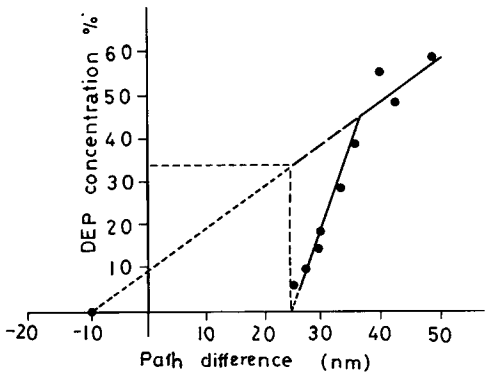

Fig. 2. Birefringence of DEP/NC (12.4% N) mixtures.

It follows that if

path difference of original NC	= −40 nm
path difference of 50% NC/NG paste	= 52 nm
critical DEP concentration for opening lattice	= (40 + 12.5) × 50/(40 + 52.5)
	= 28.4%
∴ the corresponding NC concentration	= 71.6%

Since the molecular weight of 1 unit of NC of 12.9% N is 263 and that of DEP is 222, the molar ratio DEP/NC = 0.46.

It may be shown that this figure corresponds closely to the number of unesterified hydroxyl group in the sample.

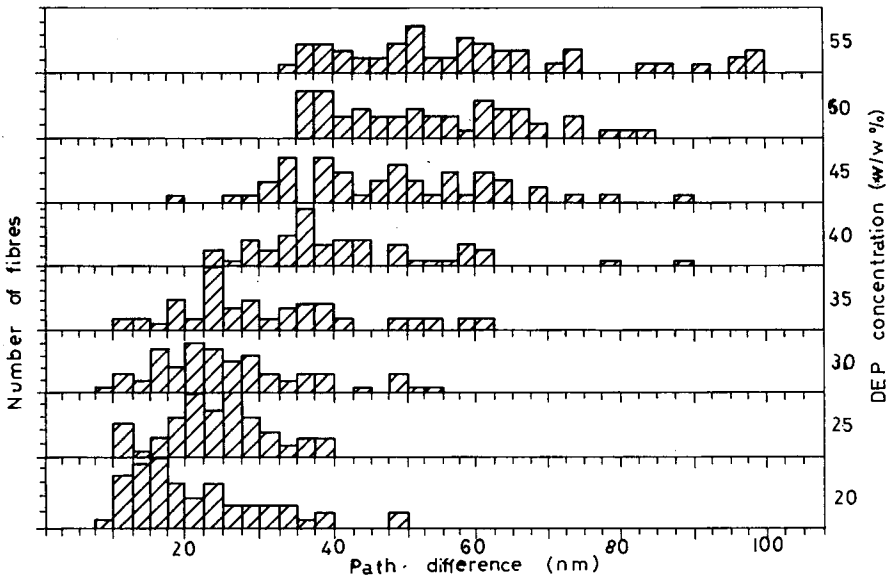

Fig. 3. Birefringence distribution of various DEP/NC (12.9% N) mixtures.

Where the number of nitrate groups per residue is q

$$q = 3.6 \times N\% \ (31.13 - N\%)$$

which, for a 12.9% N sample $q = 2.547$

$\therefore$ molar ratio OH/NC $= 0.452$

The same procedure was adopted for a series of pastes made with 12.4% N NC. The path differences are shown in Figure 2. The path differences of the NC is −10 nm, that of a 50% paste 40 nm, and that of the critical DEP concentration 25 nm. The observed critical DEP/NC ratio was 0.65, and that of the OH/NC ratio was calculated to be 0.62.

Thus it appears justified to state that the observed immobility of the boundary between swollen and unswollen material is due to the 1:1 interaction between DEP and residual hydroxyl groups in the NC. This renders the DEP inactive and further movement of the boundary can only occur if fresh supplies of DEP pass through the swollen region to attack the next unopened lattice layer. That there is specific interaction between phthalates and hydroxyl groups in NC pastes has previously been shown by changes in the OH stretching frequency in the infrared.[9]

Sorption of DEP from DEP/Benzene Mixtures

The sorption of pure DEP into NC fibers is a rapid process making quantitative kinetic measurements under the microscope a difficult procedure. In the hope of reducing boundary movements to a more manageable rate the activity of the DEP was lowered by mixture with benzene. Benzene itself has little effect on NC fibers over a matter of a few days, and has a refractive index suitable for immersion purposes. Its disadvantage is its volatility. To overcome this and to avoid unwanted and uncontrolled changes in the DEP/benzene composition on the microscope slide the following procedure was adopted.

Inert silicone grease was applied to the edges of a cover slip covering a sample of NC fibers, leaving two small unblocked regions on either side. DEP/benzene solution was added dropwise to one entrance, and as the solution moved across the slide air was forced out through the opposite exit. The two pores were then sealed with more grease. Such slides could be observed satisfactorily over a period of a few hours.

The typical sorption pattern was quite different from that of pure DEP. For compositions in the range of 30–40% DEP no lumen attack was visible and sorption occurred through the outer wall along certain lengths of fiber. A sharp boundary moved with constant velocity towards the fiber axis until a whole length of fiber became swollen. The linear motion is shown in Figure 4 and indicates a Case II mechanism of penetration. The yellow, optically positive regions then began to expand slowly along the length of the fiber, but with an indistinct and irregular boundary.

The interpretation of these observations is as follows. On first contact the lumen and the microcracks in the fiber which are known to be present are filled with DEP/benzene mixture. The DEP is absorbed by the surrounding NC lattice, leaving pure benzene filling the lumen and other pores, but insufficient DEP is absorped in this first stage for birefringence changes to be visible. Attacks on some portions of the outer wall occur and from these foci a sharp boundary between swollen and unswollen material proceeds towards the center

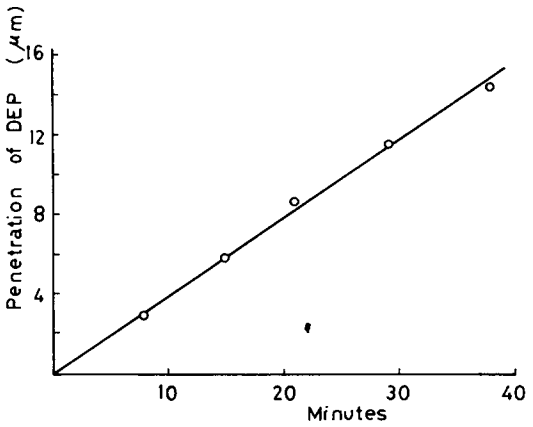

Fig. 4. Rate of penetration of DEP into fiber (40% DEP in benzene).

of the fiber by a Case II mechanism. At this stage the fiber will show alternative bands of swollen and unswollen material. The slow movement from these attacked areas along the length of the fiber is due to diffusion through the benzene-filled capillaries and subsequent sorption at their walls. This final picture of diffusion through solvent-filled microcracks is consistent with the point, developed in the following section, that neither Fickian diffusion nor Case II motion occurs through the lattice in the direction parallel to the fiber axis.

Sorption of DEP by Diffusion through Glycerol

In this experiment the rate of sorption of DEP into NC fibers was slowed down by reducing the flux, although not the activity, of DEP molecules arriving at the fiber surface. Although overall sorption rates were controlled by this flux, i.e., by the number of DEP molecules arriving at the fiber surface, the experiment gave interesting information on the sorption processes occurring within the fiber.

A sample of dry NC (12.9% N) was placed on a slide and a droplet of glycerol added which was sufficiently small that only part of the NC fibers were covered when a coverslip was put in place. DEP was then introduced around the edge of the cover glass, capillary action bringing it up into contact with the glycerol. Since these liquids are immisible a sharp boundary formed. Changes occurring in those fibers within the glycerol region were observed over a period of several days.

In the DEP layer the fibers reacted as described in the first part of this section. Within the glycerol region it was noted that after a day or so those fibers closest to the DEP/glycerol interface had swollen and had changed their optical sign, indicating that DEP was being absorbed. The line of demarcation between swollen and unswollen fibers was abrupt, and depended only on the position of the fiber relative to the DEP/glycerol interface. It passed through fiber clusters and through individual fibers, whether these were aligned parallel or perpendicular to the interface (Fig. 5), and moved with a constant velocity of about 5 μm/h away from the interface. Within a single fiber the boundary between swollen and unswollen material was sharp and was most advanced along the edges (Fig. 6).

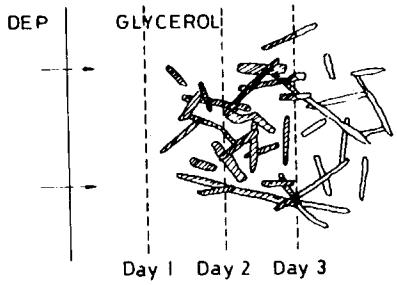

Fig. 5. Sharp demarcation between changed and unchanged fibers within the glycerol region. Shaded fibers: optically positive; unshaded fibers: optically negative.

Since isolated fibers are affected, diffusion of DEP must be through the glycerol, not along the length of the fibers. In the absence of fibers one would expect a Fickian concentration profile of DEP within the glycerol layer. However, the fact that a sharp boundary exists between positive and negative fibers indicates that sorption by the fibers disturbs this profile. DEP is absorbed up to a concentration in equilibrium with the saturated concentration in the glycerol. This equilibrium concentration within the fiber is quite high (about 50% as determined by compensation experiments and referring to Fig. 1) and indicates that the activity, if not the concentration, of DEP in the glycerol layer is high. (It cannot, of course, be considered as equal to that of pure DEP since it is in equilibrium not with pure DEP, but with a saturated solution of glycerol in DEP.) However, this is far more than is needed to saturate the hydroxyl groups in the NC, and the swollen fibers must contain excess mobile DEP. In these circumstances, if significant diffusion occurred along the length of an NC fiber, one would expect the demarcation line within a fiber perpendicular to the DEP/glycerol interface to be well in advance of the general front. This is not so, and is the most powerful evidence that, apart from capillary motion or diffusion up capillary channels, sorption movement in NC fibers is always at right angles to the fiber axis.

GENERAL DISCUSSION AND CONCLUSIONS

Despite the diversity of sorption patterns recorded in these experiments an overall picture emerges which contains no anomalies. Sorption of DEP into NC fibers is controlled by three factors:

(a) The degree to which capillary action can carry DEP through the lumen and through microcracks in the lattice, with subsequent diffusive movement through these channels.

(b) The extent to which the outer wall offers initial resistance to sorption.

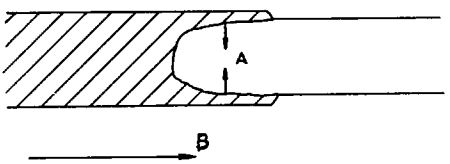

Fig. 6. Profile of DEP front within a fiber lying parallel to the diffusion direction: (A) direction of diffusion of DEP within fiber; (B) direction of diffusion of DEP through glycerol.

(c) A Case II movement through the lattice perpendicular to the fiber axis, resulting in the immobilization of DEP molecules by a 1:1 reaction with residual hydroxyl groups on the NC molecules.

Capillary movement is overwhelmingly important when the initial fibers are dry. Both lumen and lattice microcracks are affected and DEP rapidly extends from these regions to all parts of the fiber. During this time much of the outer wall remains unattacked, although in those regions of the fiber where microcracks are most important the outer wall seems to offer no protection. With NC containing 30% water (the state in which NC is normally stored and transported) many of the channels, particularly in the microcracks, are filled. However, even such fibers normally succumb to the eventual physical movement of DEP up the lumen. But if the lumen and other channels are completely filled by a liquid in which DEP is only sparingly soluble (in these experiments, water and glycerol), attack is always from the outside of the fiber. If they are filled with a liquid miscible with DEP, e.g., benzene, then there is the possibility of DEP diffusing along these channels, which allows some overall movement in a direction other than at right angles to the fiber axis.

When the lumen and microcracks are blocked, entry of the DEP has to be through the outer wall. The degree of protection given by this wall is variable. In the water slurry experiments the pure DEP appears capable of affecting all areas, and differences in the degree of penetration are more likely due to an uneven distribution of DEP over the fiber surfaces. But when the activity of the DEP is reduced by mixture with benzene, whole regions of surface become rapidly attacked whereas other regions show no attack before the whole fiber becomes swollen by diffusion through the benzene-filled lumen and microcracks.

The fact that the outer wall of an NC fiber gives protection against attack by swelling agents is well known.[10] While attack appeared to come from the damaged ends of fibers or from points where the outer wall appeared damaged, there was no need to postulate more than a physical barrier of closely packed fibrils. But the fact that sorption is rapid at the lumen surface, which we have no reason to suppose is physically damaged, and the observation of very uniform Case II boundaries which all give the appearance of moving through a continuous medium, necessitate the postulate that the surface has properties other than those of physical close packing. In 1944 a skin of un-nitrated cellulose was suggested,[11] but recent ESCA work has shown that the nitrogen content within the first 3 nm of the surface does not differ significantly from that of the rest of the fiber.[12]

Another possibility is a change in molecular alignment at the surface. This work has shown that the Case II movement takes place at right angles to the fiber axis, across molecules rather than along them. A similar effect has been noted on diffusion through films.[1] Obviously it is not possible to postulate surface molecules being perpendicular to the surface, but while directional diffusion is important there is always the possibility of some more subtle structural arrangement affecting diffusion rates.

Sharp boundary movement has been shown to occur in all cases where capillary action does not obscure the issue. In the case of DEP/benzene mixtures these have been shown to be Case II, and there is every reason to believe that a similar law applies for movement out from the lumen, or from the outside inwards in

the water slurry experiments. Indeed, this is probably the only type of movement possible in the NC lattice, even in those cases where capillary action through microcracks has greatly reduced the possible diffusion paths. Kinetics of sorption are controlled not by Fickian diffusion but by the layer-wise breaking of the hydrogen-bonded lattice. The most interesting feature is the immobility of the expanded layer if the supply of diffusant is interrupted, and that under these conditions of partial expansion a 1:1 interaction between DEP and residual hydroxyl groups occurs. This warrants further study with other diffusants; but few plasticizers, other than similar aromatics, produce sufficiently large birefringence changes to make the present technique viable.

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