# The Birefringence of Nitrocellulose Fibers and Pastes

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## Synopsis

The optical path difference of nitrocellulose fibers and pastes were measured on the polarizing microscope using three different compensation techniques, and a method is suggested for converting these path differences into birefringencies. By taking measurements on a sufficiently large number of fibers it is possible to estimate the average nitrogen content with an accuracy approaching that achieved by other methods on much larger samples. The distribution of nitrogen between individual fibers shows that material prepared by the displacement process differs from that made by the mechanical process and indicates that denitration occurs during displacement process manufacture. Solvents and plasticizers either increase or decrease the birefringence, and the structure of nitrocellulose pastes is discussed.

## INTRODUCTION

The study of nitrocellulose fibers in the polarizing microscope began early in the present century.[1] Work up to about 1955 was summarized by Miles,[2] and as recently as 1976 a paper appeared[3] in which some improvements in technique were described. All investigators are agreed that polarization colors depend on nitrogen content and that, whereas cellulose is an optically positive fiber (the high refractive index is in the direction of the fiber axis), nitrocellulose is optically negative (the fiber axis being the direction of low refractive index). Miles[2] interpreted this fact as showing that at least a majority of the highly polarizable nitrate groups must lie with their planes perpendicular to the fiber axis.

However, there are quantitative discrepancies between these various investigations far outside those to be expected from simple experimental error. For instance, Miles[2] quotes the neutral point, the nitrogen content below which the fiber is optically positive and above which it is optically negative, as occurring at 11.9% nitrogen, whereas Kohlbeck and Bolleter[3] give this point as 12.4% nitrogen. The uncertainty in nitrogen determination is about ±0.05% and cannot account for the variation between investigations. We return to this point later in discussing the origin of birefringence in nitrocellulose fibers.

The observation and recording of polarization colors is a qualitative and subjective procedure. The purposes of the present investigation have been (a) to make the study of the interaction of nitrocellulose fibers with polarized light quantitative and objective by the measurement of optical path difference on individual fibers by means of various compensating techniques; (b) to determine whether properties other than nitrogen content and fiber thickness affect the measured path difference; (c) to study the path difference variations between fibers within a single sample of nitrocellulose and to measure the distribution of the intrinsic chemical and physical structures from which these path differences arise; and (d) to observe the effect on path difference of various solvents and plasticizers sorbed into the fibers and to deduce information concerning the

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nature of the interaction between nitrocellulose and these solvent–plasticizers.

All these objectives have been achieved to a greater or lesser degree. The investigation has been in the nature of a preliminary survey, and a number of aspects justify much further study. Nevertheless, it is shown that this traditional technique is potentially one of the most powerful for deducing information concerning the structure of nitrocellulose fibers.

## EXPERIMENTAL

### Compensating Techniques

**Quartz wedge.** This will determine path differences of up to several wavelengths and is of reasonable accuracy when measuring down to $\lambda/50$, the average path difference of 12.6% N pyronitrocellulose. Higher N-content fibers may be measured, but those in the neighborhood of the neutral point, which we consider to occur at about 12.4% N, cannot really be assessed by this method. Even at the higher nitrogen level this technique was considered less accurate than the de Senarmont method described next, and hence the results for this method have not been included in Figures 1–4.

**The de Senarmont Quarter-Wave Plate.** This was the best method for measuring path differences up to half a wavelength. It was particularly suitable for nitrocellulose fibers containing more than 12.8% nitrogen. Once again, although the plate was calibrated for use with the 546-$\mu$m Hg line, and on occasion such monochromatic light was used (using an interference filter with a mercury lamp), white light was considered adequate and was much more convenient to use. The procedure was as follows. The fiber was rotated so that it was at 45° to its extinction position and lay parallel to the direction of insertion of the de Senarmont plate. The analyzer was rotated until the fiber came to extinction. The angle of rotation was proportional to path difference, a rotation of 90° being equivalent to a path difference of $\lambda/2$.

**The Rotary Mica Compensator.** This measures path differences up to $\lambda/20$ and is suitable for nitrocellulose from about 11.5% to 12.7% nitrogen. It is the only method of those tried sufficiently accurate to measure the extremely low birefringences of 12.2% nitrogen fibers. The procedure was as follows. White light was used, though monochromatic light is theoretically better. The fiber was once again aligned at 45° to its position of extinction and the rotary mica compensator inserted in the slots in the microscope tube. The compensator was rotated until extinction of the fiber occurred. The crystal was then rotated through 90° so that if it were originally parallel, it was now perpendicular to the axis of the compensator. Extinction was once again obtained by rotating the compensator. If $2\theta$ is the difference between these two positions, the path difference due to the fiber is $A \sin 2\theta$, where $A$ is a calibration factor for the instrument.

### Specimen Preparation

Most old work was carried out using glycerol (refractive index $\nu = 1.47$) as the immersion medium. This is well removed from that of the nitrocellulose fibers ($\nu = 1.52$), and much detail is lost by diffraction effects at the edges. The use

of Cargille oils[3] ($\nu = 1.51$) was found to be more satisfactory. All nitrocellulose fibers were commercial samples, dried in a vacuum oven for 45 min at 100°C. Nitrocellulose pastes were again commercial samples and were dried in air at 45°C for 20 hr.

## RESULTS

### Path Difference and Birefringence for Various Commercial Nitrocellulose Samples

After dispersion of fibers on a microscope slide in Cargille oil, measurements were made on 50 fibers from each sample by one of the compensating techniques described above. An attempt was made to include all fibers which were in a particular area of slide, but inevitably there was some subjectivity in the selection. Fifty fibers is really too small a sample for an adequate statistical analysis to be made but represented a compromise between the reward of information obtained and the tedium of effort expended. Histograms for the samples are shown in Figure 1.

The method suffers from the fundamental limitation that the measured path difference on each fiber is the product of birefringence and fiber thickness, and there is no obvious way of measuring this latter parameter. One can of course measure the lateral thickness as observed in the microscope image, but the cross sections of the fibers are not circular, and this could be quite different from the thickness in the direction of the light ray. One approach made was to assume that the statistical distribution of thicknesses in the direction of the light path was the same as that at right angles, as seen by the observer in the microscope image. There are fundamental objections to this procedure. Even if there is no tendency for the fibers to lie on their flat faces on the microscope slides, the distribution of apparent thickness of the microscopic image and that of real thickness in the light beam are rather different. The first measures the lateral difference between two extreme points even if these points are not in the same plane. This value will always be greater than the true thickness measured in a single plane. If the cross-sectional size and shape of all fibers were the same, it would be possible to calculate one distribution curve from the other. But micrographs have shown that the cross section of fibers are roughly elliptical with a range of absolute sizes and a range of eccentricities.

The distribution curve shown in Figure 2 combines all these effects. Unfortunately it was not possible to take cross-sectional measurements on the very short fibers used in this investigation. However, if it assumed that those fibers showing the greatest path difference are also the thickest in the direction of the light ray, 50 measured path differences can be placed in descending order against 50 measured fiber diameters, also placed in descending order. By pairing across and dividing the path difference by the thickness, a new distribution, that of birefringence, can be obtained. This can be seen in Figure 2 to be much sharper than the distribution of path difference. It is a matter of great interest whether this distribution of birefringence is in fact a distribution function for the nitrogen content of the fibers or whether other factors, such as the degree of crystallinity of the fiber, affect the birefringence. At least it shows that the distribution of nitrogen content is much narrower than the wide distribution of measured path differences. This point is discussed further below.

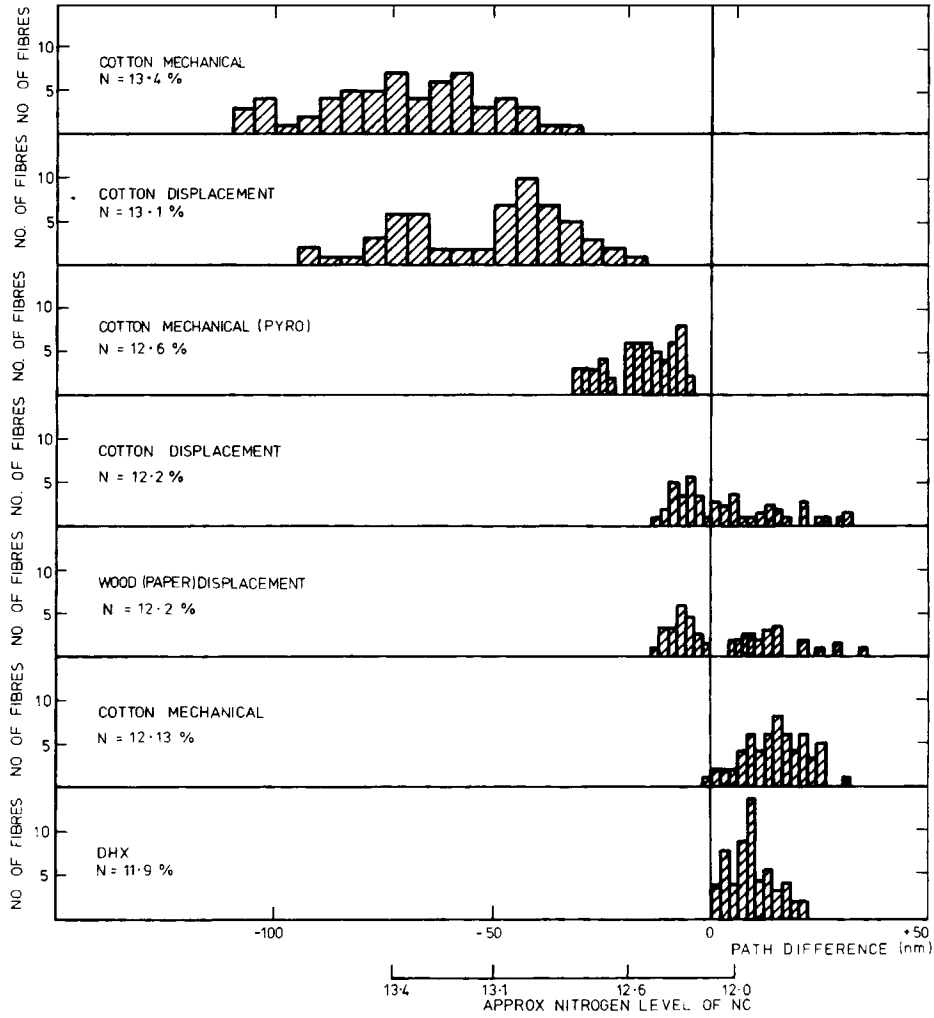


Fig. 1. Optical path difference of some nitrocellulose (NC) samples.

Despite the difficulties involved in quantitative interpretation, the following points can be made from Figure 1. It should be emphasized that the fiber thickness distribution shown in Figure 2 is the same for all types of fiber, even those derived from a wood precursor.

a. The path difference is a function of the nitrogen content of the fibers: the greater the nitrogen level, the greater the negative path difference or birefringence.

b. At the high-nitrogen end of the range there is no significant difference in the distribution of path difference between samples prepared by the displacement process from those prepared by the more usual mechanical process. This is in contrast to the observation (c) below and might indicate that at the higher nitrogen level the denitration reaction is slow.

c. At the low-nitrogen end of the range the nature of the process by which the sample has been produced has a large effect on the path difference distribution. Those samples prepared by the displacement process have a wide, bimodal dis-

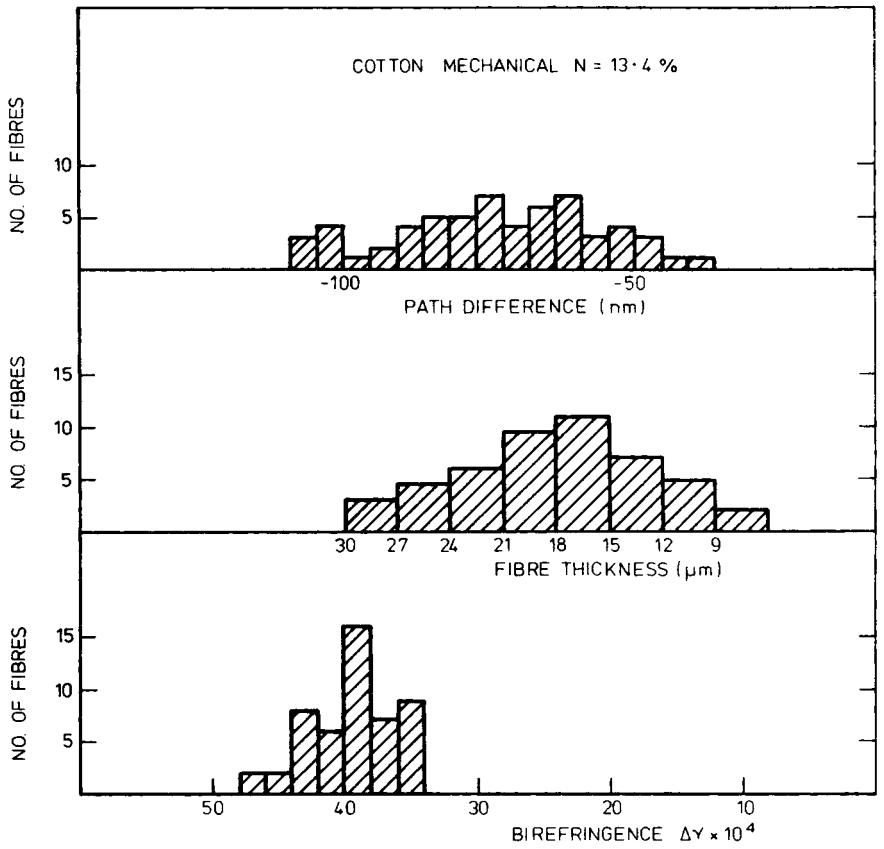


Fig. 2. Path difference, thickness, and birefringence of NC fibers.

tribution. If the path difference is proportional to nitrogen concentration, considerable denitration takes place in the displacement process. The 12.2% nitrogen displacement samples have in fact a maximum in their distribution on either side of the neutral point. This is very fortunate in some respects since, although the path difference will vary with fiber thickness, the positive or negative sign of the fiber will not change and will be a function of nitrogen content only. Thus, in studying the gelatinization process, if it is found that all positive fibers have disappeared but not the negative ones, we are on safe ground in stating that the initial attack of the plasticizer is on the fibers of lower nitrogen content. However, allowance must be made for the direct effect of plasticizer sorption on birefringence (see below). This bimodal distribution and the long tail on the low nitrogen side of the distribution curves of displacement nitrocellulose suggest that a few fibers have undergone considerable denitration and others very little. It would be interesting to know whether this was due to the position of the fibers in the displacement tank or to an inherent property of the fibers which makes some more susceptible to denitration than others.

d. No difference in optical path could be detected between wood and cotton nitrocelluloses, provided they had undergone the same manufacturing process.

e. The neutral point is at 12.4% nitrogen, in good agreement with Kohlbeck and Bolleter (12.4%).[3]

## Examination of Nitrocellulose Pastes

Paste, in this case, is the material formed when certain plasticizers, energetic or nonenergetic, dissolving or nondissolving, are sorbed into nitrocellulose to the extent that the fibrous appearance of the nitrocellulose is preserved despite the swelling which takes place. Most typical are the nitrocellulose–nitroglycerin pastes formed by mixing the two ingredients in an excess of water.

Figure 3 shows the distributions of optical path differences for a number of such pastes made up from 12.2% nitrogen, wood, displacement process nitrocellulose. The mean optical path difference of the nitrocellulose itself was −2.27 nm and that for a 50/50 NC–NG paste, −23.70 nm. Thus, the addition of nitroglycerin has increased the negative birefringence of the fibers. This is important to remember when nitrocellulose fibers are examined in propellant sections. Unchanged nitrocellulose fibers often give the appearance of being of higher nitrogen content than they really are. The addition of a third component to the paste moves the path difference back toward that of the original nitrocellulose. The addition of about 15% triacetin to the paste reduces the mean optical path difference only slightly, down to −17.30 nm, but a similar concentration of dibutyl phthalate more than compensated for the effect of the nitroglycerin and produced fibers with an average path difference of +12.2 nm. The

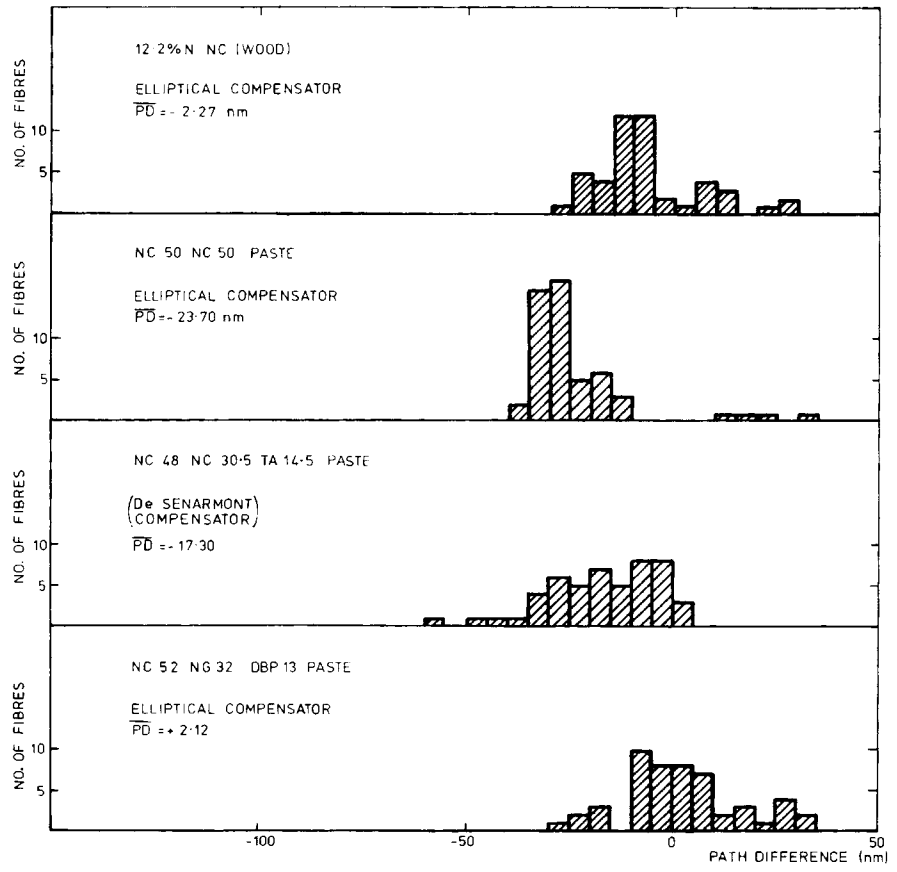


Fig. 3. Optical path difference of various NC (12.2% N) pastes.

original nitrocellulose sample and the sample of paste containing dibutyl phthalate contain an almost equal number of fibers showing blue and orange polarization colors, whereas in the NC/NG paste and the paste containing triacetin the fibers are almost entirely blue.

Figure 4 illustrates pastes made from 12.6% nitrogen pyro nitrocellulose (from a cotton linter precursor and made by the mechanical process) and nitroglycerin (NG), diethyleneglycol dinitrate (DEGDN), and triethylene glycol dinitrate (TEGDN). Once again, the addition of NG causes the optical path difference to become more negative by about 20 nm, and there is no significant difference in increasing the NG/NC ratio from about 1 to about 1.5. The negative shifts produced by DEGDN and TEGDN are rather lower than that produced by NG.

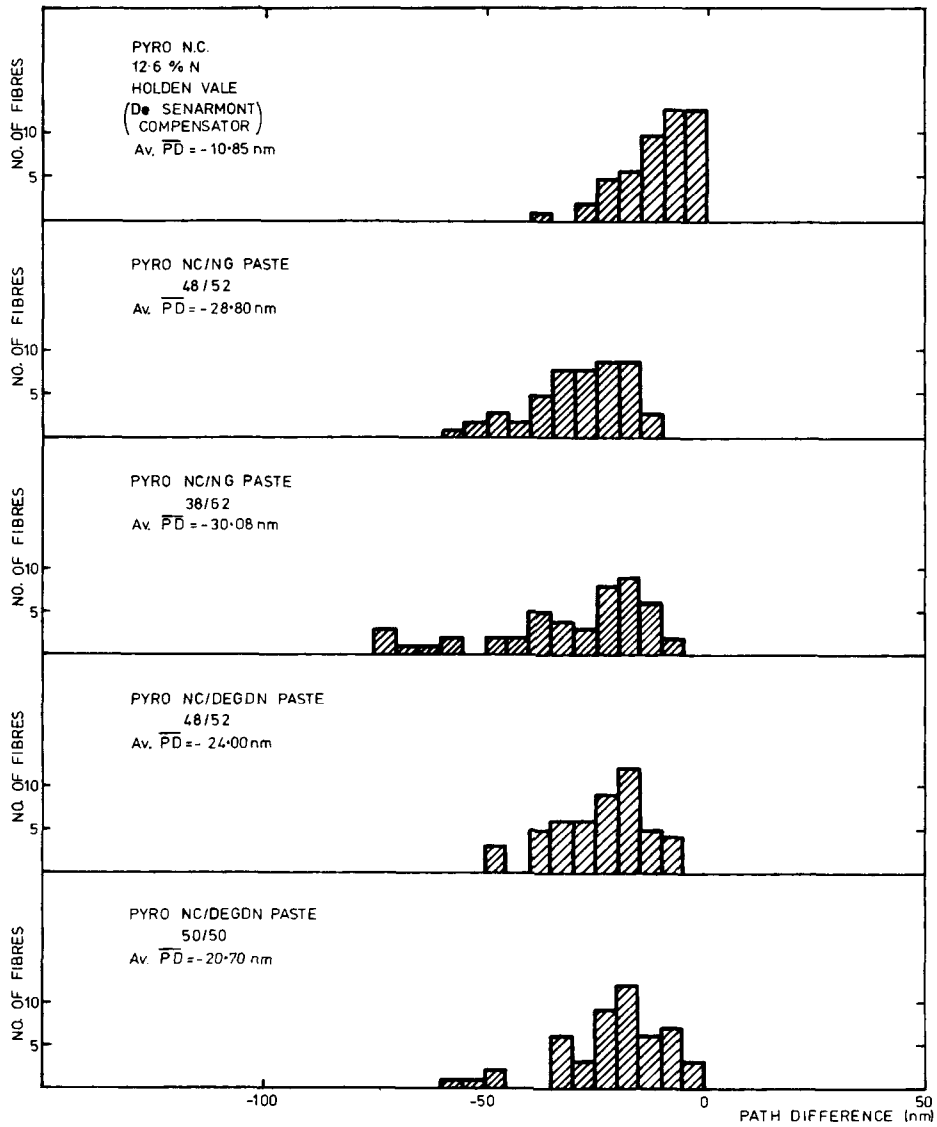


Fig. 4. Optical path difference of various NC (12.6% N) pastes.

## DISCUSSION

In assessing the value of this work, it is convenient to examine the objectives listed in the introduction and consider how far these objectivies have been attained.

The first objective—to quantify the measurement of optical path difference on individual fibers—has clearly been achieved. There are a number of difficulties, mainly due to the irregularity of the fibers. Frequently the measured path difference is different at various parts of the fiber, and even the position of extinction may vary either along the length or breadth of a fiber. Most of these variations are due to variations in the depth of the fiber in the direction of the light path and to the general convoluted appearance of many of them. The difficulty of measuring fiber depth is inherent in the method. This makes the calculation of birefringences from optical path differences an inexact procedure. However, Figures 5 and 6 show that if average path difference is plotted against the known nitrogen content of the sample, a linear relationship is obtained. Each point on Figure 5 represents results on different batches of nitrocellulose, not repeats on the same batch. Such repeats on the same batch normally gave average path differences within 0.5 nm of each other. This suggests that the average figure obtained microscopically on about 50 $\mu$g material is as accurate as the nitrometer reading, which requires about 1.0 g material.

The second objective—to determine whether properties other than nitrogen content and fiber thickness affect path difference—has not been accomplished. It was hoped to gain some idea of the crystallinity of the fiber, but the range of

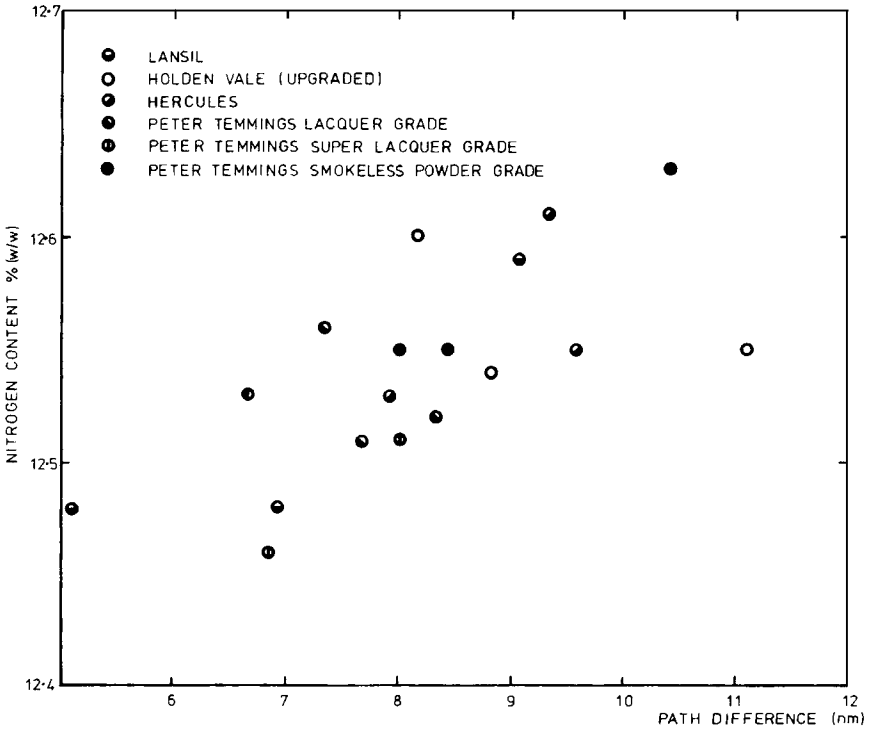


Fig. 5. Correlation between measured path difference (average for 30 fibers) and the nitrogen content for samples of pyro-NC (12.6% N) prepared from linters from various sources.

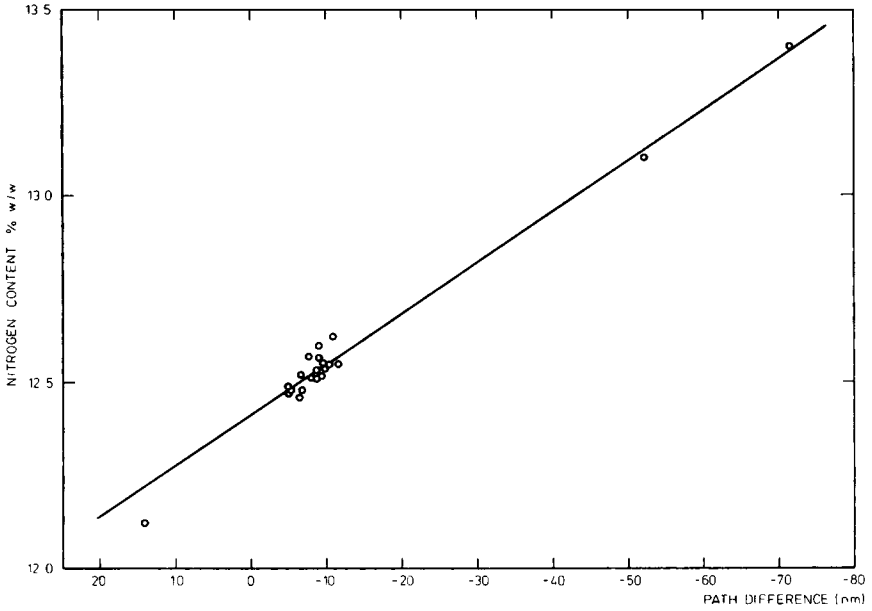


Fig. 6. Average path difference for various nitrogen contents.

optical path differences due to different fiber thicknesses is so large that crystallinity effects are likely to be masked. It might be possible to say that if a point fell very far off the regression line through the points of Figure 5 and there was no reason to suppose that there was anything unusual about the average fiber thickness of this particular sample, then its unusual path difference could be due to some other unconsidered factor. One point did indeed appear abnormal—that of having an average optical path difference of 11.1 nm but a measured nitrogen content of only 12.55%. We are examining this sample for further evidence of abnormality.

It might be appropriate at this stage to say a brief word about the origin of birefringence in a molecular solid such as nitrocellulose. It must not be assumed from the mention of the "degree of crystallinity" in the preceding paragraph that long-range crystal order is necessary in order to achieve birefringence. Miles[2] gave the precise requirement that a majority of the nitrate groups lie with their planes perpendicular to the fiber axis. The highly polarizable electrons will be those on the oxygen atoms of the nitrate groups. Dipoles are set up by the electric vector of the light beam, and these dipoles will reinforce or depress each other according to whether they are predominately line-ahead or line-abreast of each other. Free rotation around either the C–O or the O–N bond would destroy the birefringence though not of course the enhanced isotropic refractive index, which is a function of the polarizability of the isolated oxygen atom, independent of position. Restricted rotation around either of these bonds could be due to crystal forces or to steric hindrance within the molecule. Examination of molecular models shows that internal restriction is inevitable. Consequently all that need be postulated for birefringence is a general alignment of molecules, and no lateral order is necessary other than that concerning the nitrate groups referred to above. It does however seem probable that birefringence would be greater in a crystalline than in an amorphous fiber.

The third objective—the study of property distributions between fibers of a single batch—has had limited success. Obviously, optical path difference distributions can be obtained; they are the essence of the exercise. But to obtain from these the distribution of nitrogen content between fibers involves highly questionable procedures, and the second histogram of Figure 2 must be treated with some reserve. However, it is undoubtedly possible to distinguish between displacement and mechanically prepared samples, at the 12.2% nitrogen level at least. Practical differences between material prepared by these two processes have long been recognized and the apparently correct explanation postulated, but no test has previously been devised either to test the hypothesis or to distinguish between the two types of material in the laboratory.

Finally we come to the effect on path difference of various solvents and plasticizers. It has been shown that care must be taken in deducing information about nitrocellulose fibers observable in thin propellant sections. The most interesting observation is that of the increased negative path difference when nitroglycerin is sorbed into the nitrocellulose. It might be expected that plasticizers, by releasing the molecular chains, would decrease birefringence, in this case by increasing the probability of rotation of the nitrate groups of the nitrocellulose. The fact that the opposite occurs shows that the addition of nitroglycerin either holds the nitrate groups of the nitrocellulose more firmly perpendicular to the fiber axis or that there is an ordered solvation in which the nitrate groups of the nitroglycerin are themselves aligned so that their nitrate groups are horizontal to the axis of the nitrocellulose. It is known[4] that the addition of nitric esters does not alter the dimensions of the unit cell of nitrocellulose, as measured by x-ray diffraction. It is reasonable to suppose that plasticizers are absorbed only into the amorphous regions of the fiber and do not penetrate into the ordered lattice. It must therefore be the birefringence of the amorphous region of nitrocellulose which is enhanced. A similar effect has been reported by Vermaas,[5] who, working with fibers of nitrated regenerated cellulose, 0.2 mm thick, found that birefringence varied with the nature of the immersion liquid. As in the present study, he found both positive and negative shifts in the birefringence, aromatic liquids being particularly effective in changing an optically negative fiber into an optically positive one. This agrees with our own results on dibutyl phthalate pastes. Vermaas interpreted his observations in terms of alignment of solvent molecules, although the alternative interpretation mentioned above (enhanced rotation of the nitrate groups in nitrocellulose) is still possible.

To end this discussion, mention should be made of a paradox. Cellulose fibers are built up of fibrils about 1 $\mu$m in diameter, which are themselves constructed of microfibrils down to the ultimate microfibril about 3.5 nm in diameter. These fibrils are wound helically to form the fiber. Except at intervals along the cotton fiber where the direction of the helix changes and for a short period the fibrils are aligned to the axis of the fiber, it is not possible to obtain extinction under crossed nicols. This is because the fibrils in the near side of the fiber will be sloping in the opposite direction from those same fibrils on the lower half. There is no way in which plane-polarized light can pass through the fiber without producing a component at right angles to the original plane of polarization. Nitrocellulose, on the other hand, gives good extinction and has all the appearances of a single, if irregular, crystal. The unwinding of the fibrils during ni-

tration seems improbable. There is an outer wall in which two sets of fibrils wind in opposite directions, and this gives rigidity to the fiber. And the appearance of the nitrocellulose, apart from swelling, seems too similar to that of the original cellulose for such a large morphological change to have occurred. But we have no other explanation to offer for this phenomenon.

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