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Temperature effects on the birefringence of nitrocellulose and nitrocellulose/nitro-glycerine mixtures

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Changes in the optical path difference of nitrocellulose fibres of varying degrees of substitution over the temperature range −120°C to 130°C are interpreted as due to conformational changes in the primary nitrate group. Changes in path difference of nitrocellulose/nitroglycerine paste fibres over the same temperature range indicate an irreversible annealing effect and a change in the nitrocellulose structure. Propellants made from nitrocellulose and nitroglycerine show similar changes and it is concluded that submicroscopic fibrils are present even though no fibres are visible. When fibres are visible they show a banded structure, the nature of which is discussed.

INTRODUCTION

It has long been known that the colour of nitrocellulose fibres viewed under crossed polars depends upon their degree of substitution[1]. These colours are anomolous and do not follow the normal first order sequence[2]. At a nitrogen level of about 12.3% (degree of substitution, $DOS,=2.35$) the fibres are isotropic. At higher nitrogen levels the fibres appear blue, and at higher nitrogen levels still, (above 13.0%), silvery white. In this range the birefringence is negative, i.e. the high refractive index is at right angles to the fibre axis. At nitrogen levels below 12.3% the fibres appear yellow and are optically positive. Although this difference in the polarization colour on either side of the neutral point is anomolous, the blue to yellow transition makes a very convenient end-point when using optical compensators with white, rather than monochromatic, light. The quantitative relationship between the average path difference of a fibre (and, with some assumptions, its birefringence) with nitrogen content has been established[3], and the variation in birefringence with nitrogen content has been used to obtain information concerning the conformation of the substituent nitrate groups[4].

The sorption of plasticizers changes the birefringence of nitrocellulose fibres[3]. Nitric esters, such as nitroglycerine, increase the negative birefringence, and the fibres appear more blue or more white than their nitrogen content would warrant. On the other hand, plasticizers containing an aromatic ring, (such as ethyl phthalate), will convert a strongly negative, blue, fibre into an optically positive, yellow, one[5]. This is presumably due to the alignment of the aromatic rings parallel to the fibre axis.

There is much interest in the study of molecular transitions in plasticized nitrocellulose systems since these control the important mechanical properties of propellant systems. A transition below room temperature (the β transition) has been studied by dielectic spectroscopy[6], and is believed to be associated mainly with rotation of plasticizer. Dynamic mechanical analysis (DMA) has been found to be the most effective technique for studying transitions above room temperature (the α transition)[7], and here the movement may be due to that of the polymer chains, influenced, of course, by their plasticized environment.

However, it is rarely possible to make an unequivocal molecular interpretation of a dynamic relaxation process. Independent structural information will help, but the nature of the system limits available techniques. Birefringence, which is intimately related to molecular conformation, offers some prospect, and studies have been made on the variation of birefringence with temperature over a range (-120°C to $+130$°C) wherein the main dynamic relaxations are known to occur. This paper presents the results of these studies. Three types of system have been investigated (a) unplasticized nitrocellulose fibres of various nitrogen contents, (b) fibres into which nitroglycerine has been absorbed but which still retain the same overall appearance as the original nitrocellulose fibres (NC/NG paste, in the terminology of propellant chemists), and (c) nitrocellulose/nitroglycerine systems which have been partially homogenized by solvent treatment.

Depending on the composition of the solvent used these treated samples (c) may contain no fibres visible in thin sections (5 μm) under the optical microscope. Others may contain many residual fibres, the optical properties of which are somewhat different from those of the untreated, plasticized fibres (b). These last samples (c) may be regarded as characteristic of the structure of nitrocellulose-based propellants.

EXPERIMENTAL

The nitrocellulose was of three types, each being a commercial sample of the principal grades used in UK propellant manufacture.

(a) Material of 12.2% nitrogen ($DOS = 2.35$) manufactured from wood pulp by the displacement process at the Royal Ordnance Factory, Bishopton.

(b) Material of 12.6% nitrogen ($DOS = 2.45$) manufactured from cotton linters by the mechanical nitration process at the Nobel Explosives Company, Stevenston, Ayrshire.

(c) Material of 13.4% nitrogen ($DOS = 2.72$) manufactured from cotton linters by the mechanical nitration process at the Royal Ordnance Factory, Bishopton.

Although there is a difference in the evenness of nitration between the displacement and mechanical processes[3], there is no reason to believe that this unevenness applies to individual fibres. In addition, although wood pulp is generally regarded as less crystalline than cotton, we have been unable to detect differences in the birefringences of nitrocelluloses derived from the two sources.

Nitroglycerine was obtained by aqueous extraction from dynamite supplied by the Royal Ordnance Factory, Bishopton.

Nitrocellulose fibres plasticized with nitroglycerine (NC/NG paste) were made by mixing the two ingredients in a large excess of water.

All samples of NC and NC/NG paste were dried at room temperature under vacuum.

Samples of compacted, homogenized NC/NG were made by the normal techniques of propellant production. This involved mixing with an acetone/ethanol solvent of such a composition and quantity that an extrudable dough was obtained. Extrusion into strands was followed by hot air drying. Thin sections, either 5 or 10 μm, were taken parallel to the extrusion direction.

All specimens, whether nitrocellulose, nitrocellulose/nitroglycerine paste, or propellant were mounted in Cargille oil with a refractive index of 1.52. The optical compensator techniques have been previously described[3]. A rotary mica compensator was used for the low path differences (up to 20 nm) associated with 12.2% N nitrocellulose; for larger path differences a de Senarmont compensator was used.

The cold/hot stage was a TH600 supplied by Parr Scientific Ltd, Raynes Park, London. This consisted of a central silver block surrounding a sapphire window. This block contained a heating element, a platinum resistance thermometer, and a conduit for the passage of cold nitrogen gas. The specimen, mounted in Cargille oil between two cover slips was placed directly over the sapphire window. The block was surrounded by an aluminium casing with glass windows through which was passed dry nitrogen. Heating was under microprocessor control. Heating rate was normally 10°C/min, but held constant every 10°C for several minutes whilst several readings were taken. In practice in all experiments below ambient temperature all but fine control over temperature was achieved by altering the rate of flow of cold nitrogen gas, thereby minimising temperature gradients within the silver block.

RESULTS AND DISCUSSION

Birefringence of NC fibres: effect of NG sorption

Figure 1 shows the effect at room temperature (about 20°C) of various amounts of absorbed nitroglycerine on the optical path difference of nitrocellulose fibres (12.2% nitrogen). Each point represents an average value measured on 40 fibres. Although it is usual to express nitroglycerine content as a percentage of total weight, it is here expressed as a percentage of the nitrocellulose content. It must be remembered that in looking at a single fibre the average amount of nitrocellulose in the light path will be the same whatever the amount of nitroglycerine absorbed.

Concentration, as plotted in this manner, is a measure of the additional material in the light path. If there is no anisotropy in the plasticizer and no change in molecular conformation of the nitrocellulose the path difference will be unaltered, although, because of swelling, the birefringence will fall. The fact that path difference changes markedly means that one of two effects must occur; either the nitroglycerine is so aligned that, on average, the planes of its nitrate groups lie at right angles to the fibre axis, or there is increased alignment of the planes of the nitrate groups of the nitrocellulose, again at right angles to the fibre axis. Whichever mechanism is occurring, the effect of a standard increment of nitroglycerine is greatest at low concentrations. Above about 100% nitroglycerine (50% as a percentage of total weight) further addition has little measurable effect on the path difference.

There is evidence from other techniques that the sorption of nitroglycerine becomes progressively weaker at higher concentrations. Dielectric spectroscopy shows that the relaxation of the nitroglycerine (12:2% nitrogen) becomes progressively slower up to a concentration of 27% (based on total weight), but thereafter rapidly increases in frequency[6]. Examination of the spin-spin relaxation times (T_2) in proton magnetic resonance indicates a 'solvation limit' of 33% nitroglycerine (based on total weight) for a nitrocellulose sample containing 12.5% nitrogen[8]. Below this limit the nitroglycerine is
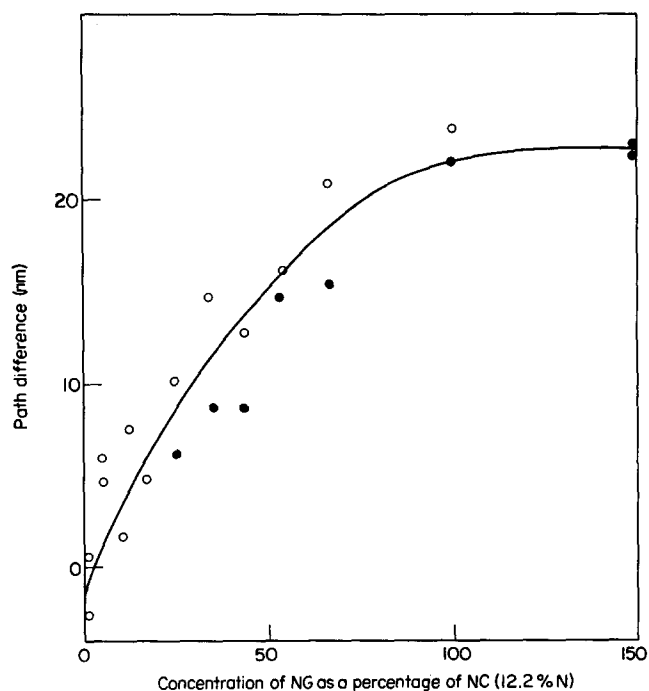
Figure 1 Effect of NG sorption on optical path difference. (O) Rotary elliptical compensator. (●) de Senarmont compensator

immobile. Measurement of vapour pressure over an NC (12.0% nitrogen)/NC system[9] showed that at 60°C the vapour pressure of a 45% nitroglycerine sample (based on total weight) was the same as that of pure nitroglycerine, but at lower concentrations decreased sharply. At the lowest temperature studied (43°C) the transition was less sharp. At 45% nitroglycerine vapour pressure was about 90% of that of the free liquid. The vapour pressure of pure nitroglycerine was reached at a concentration of about 60% (based on total weight).

The general picture emerges of three main regimes for the nitroglycerine[8]. Below about 30% it is strongly held and immobile. Between about 30 and 50% it becomes mobile but does not have the properties of the pure liquid. Above about 60% the thermodynamic behaviour is that of the pure component and the system may be regarded as two-phase. But the transition between each of these regimes is not sharp and sudden changes in properties are not to be expected.

This picture is supported by the present birefringence studies if the path difference changes are interpreted as being due directly to the nitroglycerine and not to a modification of the birefringence of the nitrocellulose. The constancy of the path difference above 50% (based on total weight) is obviously compatible with the model of nitroglycerine acting as a free liquid in this region. Within the accuracy of our experiments it is not possible to detect a definite change in shape in the 30% region. What can be concluded with certainty is that between 30 and 50% the nitroglycerine, even though mobile, still has a preferred orientation with the plane of the nitrate group at right angles to the fibre axis.

It is tempting, though probably unjustified, to draw from these data conclusions concerning the nature of the solvation between nitrocellulose and nitroglycerine. A 46% nitroglycerine sample has a molecular ratio of one to one between the nitroglycerine and the sub-molecule of the nitrocellulose, and some form of complex could exist. But it is known that the addition of nitroglycerine and alkyl nitrates in general does not alter the nitrocellulose unit cell as determined by X-ray diffraction[10]. This is in contrast to the effect of ketones and organic esters, where a regular increase in the size of the unit cell is observed with increasing solvent absorption. Clearly the crystalline part of the nitrocellulose fibre is inaccessible to nitroglycerine, and unless the extent of this is quantitatively known no conclusions can be drawn concerning the molecular significance of the critical NC/NG ratios. A model in which the nitroglycerine regimes are interpreted as mono-layer and multi-layer adsorption on to crystalline nitrocellulose micro-fibrils is probably more realistic, and has recently been discussed in some detail[6].

Birefringence of NC fibres: effect of temperature

Figure 2 shows the effect of temperature on the path difference for nitrocellulose fibres of the three types studied (Nitrogen content—13.4, 12.6 and 12.2 respectively). Because of the time required for each temperature cycle each curve is an average of only four or five fibres. The absolute values for path difference will be less accurate than those in *Figure 1*, which involved averaging over 40 fibres, but the precision of the changes with temperature will be high. These curves do not change on repeated temperature cycling, and there is no hysteresis between the effect of temperature when moving

in an upward compared with a downward direction. In summary:

(a) All temperature induced changes in structure are reversible.

(b) Structure, as defined by the lateral planar alignment of the nitrate groups, is lost as the temperature is increased from 0°C to 120°C.

(c) Structure changes are occurring at low temperatures. There is a maximum in the optical path difference at about −60°C.

(d) The structure is at its most ordered below −100°C and again at about 0°C. The path difference in these two regions is about the same.

(e) The nitrogen content of the NC has little effect on the observed changes with temperature.

The loss of structure at temperatures above 0°C is not particularly surprising. It is clearly not due to a loss of alignment of long molecular segments. If this were happening one would expect the curves for the three different nitrogen levels to converge with rise in temperature. The greater the initial birefringence the greater the changes produced by disorientation. The parallel nature of the curves would suggest that changes are occurring in the orientation of a specific group which is common to all three types of nitrocellulose. The most likely candidate is the primary nitrate group. The
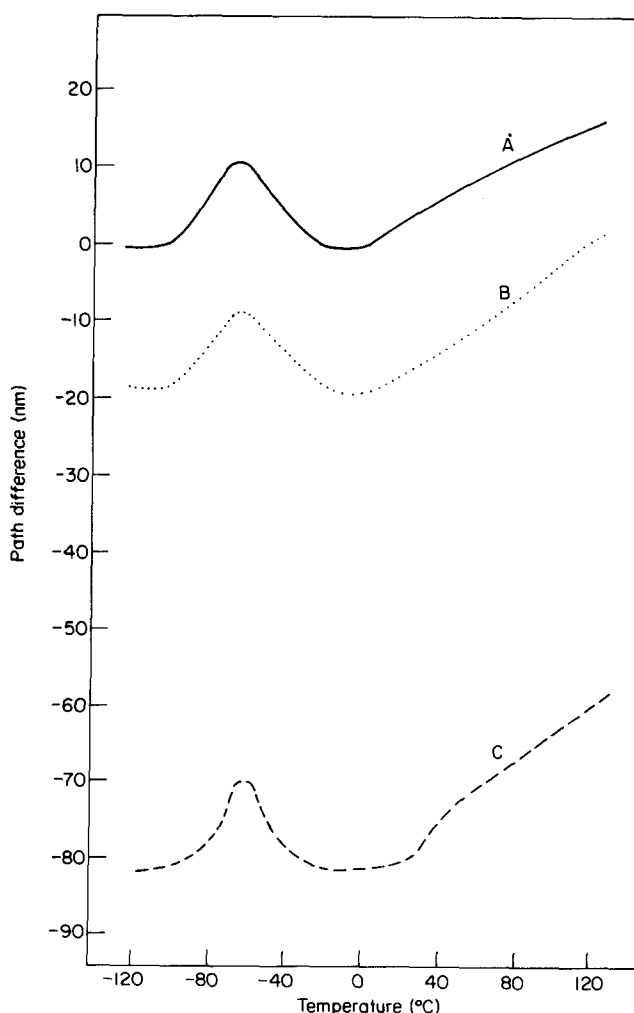

Figure 2 Effect of temperature on the optical path difference of NC fibres. A, 12.2%N; B, 12.6%N; C, 13.4%N
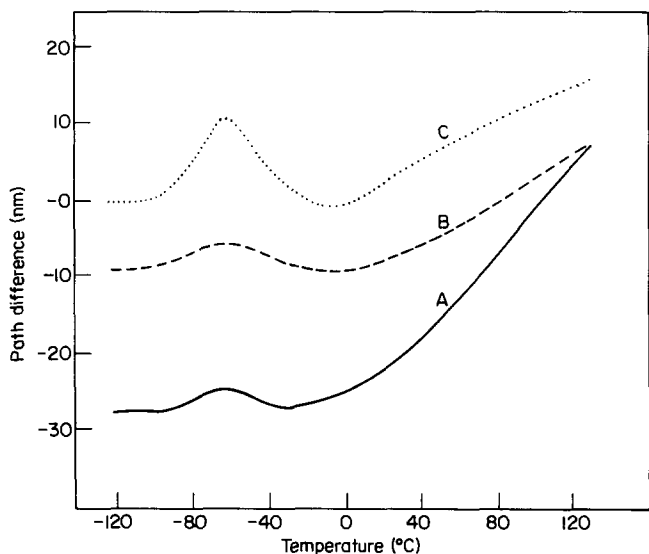
Figure 3 Effect of temperature on the optical path difference of NC (12.2%N) and NC (12.2%N)/NG paste fibres. A, NC/NG (1:1), first heating curve. B, NC/NG (1:1), first cooling, and subsequent heating and cooling curves. C, NC alone

hydroxyl group attached to C(6) in cellulose is known to be the first to be substituted, and the number of primary nitrate groups in nitrocellulose will not change markedly over a range of total substitution 2.35 to 2.72[11].

The variation of path difference with temperature below 0°C is more complex. A change was expected from one level of birefringence to another at a temperature which coincided with the peak in the dielectric spectrum (about $-40°C$ at 10 KHz, at considerably lower temperature under the static conditions of the present experiments). What was not expected was a maximum in the birefringence between two temperature regions of high and similar order. This apparent anomoly can be resolved when it is considered that path difference (or birefringence) is not necessarily a direct measure of 'order'. In the case of nitrocellulose a high negative birefringence results from the plane of the nitrate group being, on average, at right angles to the fibre axis. A highly ordered structure could occur without this particular alignment. In fact it has been shown[4] that of the three possible conformational positions of the primary nitrate group, tg, gt and gg, only the first two will contribute to the negative birefringence, and by an approximately equal amount. In the gg position the plane of the nitrate group tends to be parallel to the fibre axis and will hence enhance *positive* birefringence. The path difference changes observed in passing from $-100°C$ up to 0°C could be explained if the primary nitrate group undergoes a series of conformational changes tg–gg–gt or gt–gg–tg. If these conformers can be treated as at equilibrium, and if it is assumed that NC_{tg}/NC_{gt} at $-100°C$ is 0.9 and at 0°C 0.1, then ΔH, the enthalpy difference, is about 2 kcal mole^{-1}, which is a very reasonable value. The enthalpy of the gg conformer is intermediate between the two.

Birefringence of NC/NG fibres: effect of temperature

Figure 3–5 show the effect of temperature on the path difference of fibres into which an equal weight of nitroglycerine has been absorbed. (50% NC/NG paste.) It should be emphasized again that apart from an increased

width there is little difference between these fibres and that of the parent nitrocellulose. The convolutions typical of cotton and sundry surface features are retained. The negative birefringence of all types of NC is increased, indicating that the effect of plasticizers shown in *Figure 1* is not limited to any particular nitrogen content.
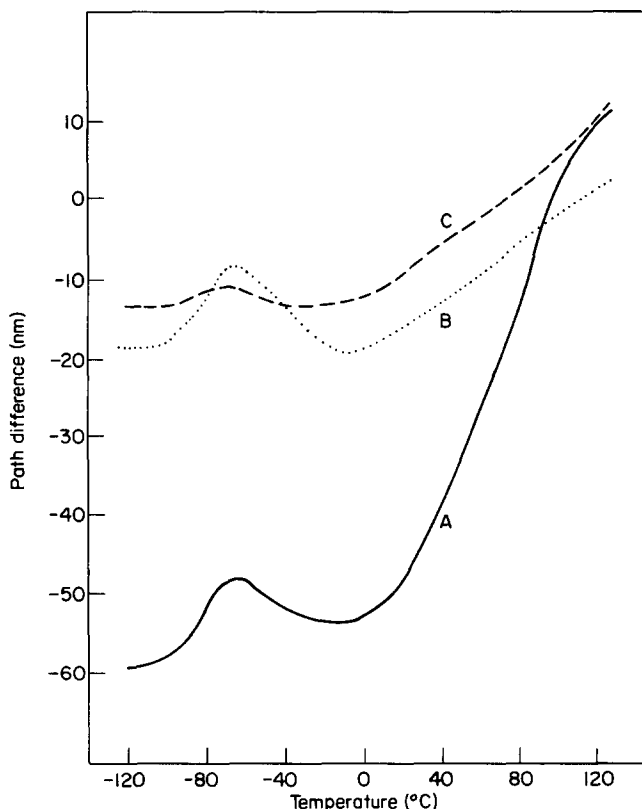

Figure 4 Effect of temperature on the optical path difference of NC (12.6%N) and NC (12.6%N)/NG paste fibres. A, NC/NG (1:1), first heating curve. B, NC/NG (1:1), first cooling, and subsequent heating and cooling curves. C, NC alone
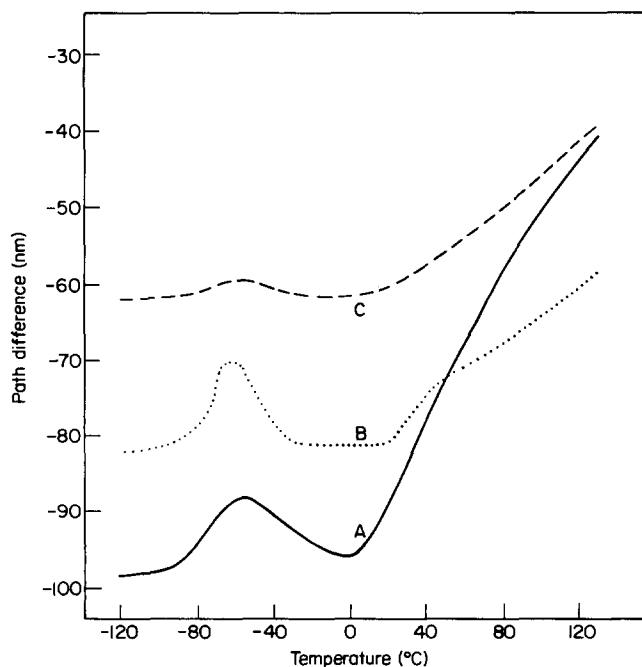

Figure 5 Effect of temperature on the optical path difference of NC (13.4%N) and NC (13.4%N)/NG paste fibres. A, NC/NG (1:1), first heating curve. B, NC/NG (1:1), first cooling, and subsequent heating and cooling curves. C, NC alone

All samples show an irreversible annealing effect. Much negative birefringence is permanently lost during the first heating stage, resulting in a cooling curve considerably displaced from that of the first heating curve. Subsequent heating and cooling cycles on the same fibre simply retrace the first cooling curve. Little significance should be placed on the indication that at 120°C the path difference of a 50% NC/NG fibre is less than that of the corresponding nitrocellulose. Too few fibres have been measured (3–5 for each curve) for this to be stated with any confidence. But the measured effect of temperature on any one fibre is precise, and it is reasonable to use the difference in the measured path difference at −120°C before and after temperature cycling as a measure of the annealing effect. On this criterion the annealing effect is higher in 12.6 and 13.4% nitrogen pastes than it is in 12.2%. At −120°C for a 12.2% nitrogen 50% NC/NG paste the difference between the annealed and unannealed curve is only 25 nm, whereas for 12.6% nitrogen NC/NG it is 46 nm and for 13.4% nitrogen it is 49 nm. Apart from this loss of negative birefringence a further effect of annealing is to greatly reduce the peak which occurs at −60°C. Even in the unannealed curves there is a tendency for this peak to be lower and broader than in the corresponding nitrocellulose, this effect being most noticeable with 12.2% nitrogen NC. After annealing the peak is barely perceptible.

In the discussion of *Figure 1* it was maintained that the enhanced path difference which occurs on the absorption of nitroglycerine is more likely to be due to an alignment of the plasticizer molecules rather than to a change in the structure of the nitrocellulose. It would appear that the reverse is happening in the case of annealing. The loss of the peak at −60°C can realistically only be explained by postulating that nitrocellulose, when plasticized by nitroglycerine, does not go through the series of conformational changes that occur in the unplasticized material. Any other explanation would require nitroglycerine to go through conformational changes at −60°C which were equal and opposite in their effect on birefringence to those undergone by nitrocellulose. This seems improbable.

Birefringence of propellants: effect of temperature

Two series of partially homogenized and extruded NC/NG mixtures were examined. One series was made from 12.2% nitrogen NC and the other from a mixture of 12.6% and 13.4%. Each series contained various amounts of nitroglycerine, and each sample was treated in an incorporator with acetone/ethanol mixtures of various concentrations in order to obtain an extrudable dough. Each sample contained 1% diethyldiphenylurea as stabilizer. These samples were effectively propellants even though some of the compositions and conditions of preparation were outside the range normally used in large-scale manufacture.

In the propellant industry the term 'gelatinization' is used to describe the extent to which undispersed nitrocellulose fibres are visible when propellants are examined in thin sections (5–10 μm) in polarized light. Although regarded as an important property affecting both ballistic and mechanical behaviour, it has never been put on a satisfactory quantitative basis. In the present study structures were seen which ranged from the totally fibrous, in which no areas of structureless matrix could

be isolated to the totally gelatinized, in which no fibres were visible. The dependence of these structures on composition and processing presented no surprises. Gelatinization (i.e. extent of homogenization) was

(a) greater with 12.2% nitrogen NC than with the 12.6/13.4% blend,

(b) greater the more acetone was present in the solvent mixture, and

(c) greater the more nitroglycerine was present in the composition (a small effect).

All these effects are well known to propellant chemists.

In the present study two aspects were singled out for more detailed examination. Both throw considerable light onw hat is clearly a highly complex multi-phase system. The first study was that of the residual fibres in a partially gelatinized propellant. Large differences were observed between these fibres and the NC/NG paste fibres before incorporation into propellant. These differences went far beyond that of simple mechanical break-up. The second study was that of the birefringence shown by an apparently homogeneous matrix. This birefringence is only apparent in highly gelatinized specimens. When an appreciable number of fibres are visible the matrix appears isotropic. In the interpretation of our data we have been well aware that cellulosic systems frequently show liquid crystal structures. It has been of particular interest to assess the potential of the liquid crystal concept in the elusive description of propellant structure.

Figure 6 shows a typical residual 13.4% nitrogen fibre in a propellant containing 60% nitroglycerine, and processed with a 30/70% w/w acetone/ethanol mixture. Although surrounded by many smaller fibre fragments, the central large fibre can be seen to be quite different in appearance from that of the unprocessed paste. Individual paste fibres behave as single crystals, extinguishing along the whole length of the fibre when aligned with the polars. This fibre, which is typical of the vast majority of fragments long enough to be termed 'fibres', extinguishes in a series of lateral bands, the position of which move as the polarizer and analyser are rotated in unison. The banded structure is most apparent when the polarizer is at about ±30° to the fibre axis. Contrary to normal NC or paste fibres, there is almost no extinction when the fibre is directly aligned with the polarizer. The bands are not regular, but have a repeat distance of about 2–5 μm. They
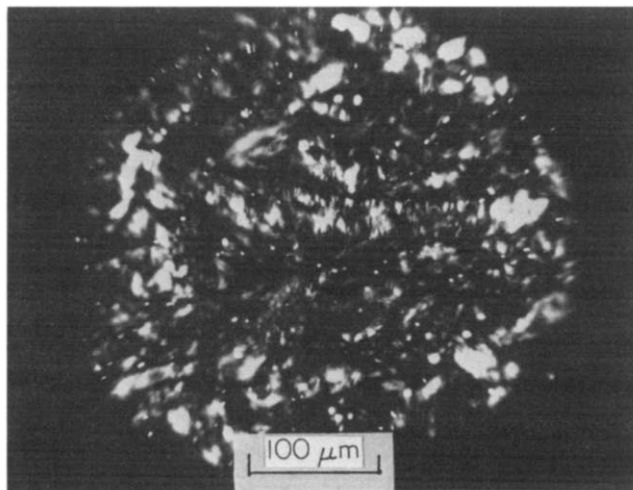

Figure 6 An NC (13.4%N) fibre just prior to gelatinization showing banded structure
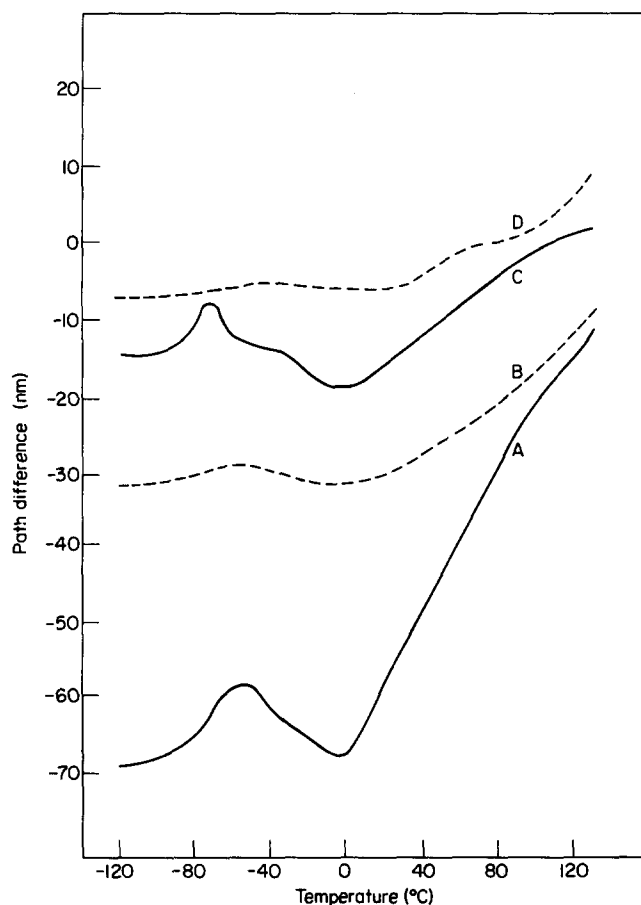
Figure 7 Effect of temperature on the optical path difference of gelatinized propellant. A, Propellant made from 13.4%NC, first heating curve. B, Propellant made from 13.4%N NC, first cooling, and subsequent heating and cooling curves. C, Propellant made from 12.2%N NC, first heating curve. D, Propellant made from 12.2%N NC, first cooling, and subsequent heating and cooling curves

are not confined to high nitrogen nitrocellulose. 12.2% nitrogen fibres show similar behaviour under certain conditions of processing, though the intrinsically low birefringence from such fibres make their photographing less satisfactory.

Banded structures have been recorded by polarized light microscopy for a number of different polymeric fibres and films. Highly crystalline polyamide fibres of the Kevlar type show close banding at a separation of about 1 μm[12]. Although prepared from a mesomorphic solution the banded appearance of these fibres is probably a consequence of their 'pleated sheet' crystal structure[13]. Very similar banded structures have been seen in a series of thermotropically prepared copolyester fibres[14]. These authors considered that the banded structure lying perpendicular to the shearing direction is a feature characteristic of oriented liquid crystalline polymers in general. Banding rather similar to that seen in the present study with repeat distances of 5 μm or so have been reported for hydroxypropyl cellulose and cellulose diacetate films prepared under certain conditions[15]. Again, these authors considered such banding to be characteristic of a liquid crystal structure.

The examples cited in the previous paragraph were prepared from molecularly dispersed solutions or from the melt. That such banded structures can arise also from a semi-natural plasticized fibre when subjected to shearing forces is a matter of some interest. There is no reason

to suppose that the changes in the optical director along the length of the fibre reflect other than the direction of the cellulosic chains, and the formation of a pleated structure somewhat analogous to that of Kevlar seems to be the inevitable conclusion.

As has been stated above, the appearance of birefringence in the apparently homogeneous matrix occurs only in highly gelatinized samples and coincides with the final disappearance of visible fibres. Areas extending over several hundred microns extinguish simultaneously as the stage is rotated between crossed polars, and within these domains alignment is effectively complete. *Figure 7* shows the effect of temperature on this background birefringence for a sample prepared from a mixture of 12.6 and 13.4% nitrogen nitrocellulose. Although the absolute path differences are lower the effect of temperature is identical to that on a 13.4 NC/NG paste (*Figure 3*). The loss of negative birefringence at $-60°C$ and again above room temperature is the same, as is the annealing effect. The fact that above room temperature the birefringence does not fall to zero but falls by the same proportion as does the path difference in a 13.4 NC/NG paste fibre indicates that the same process is happening in each. The loss of birefringence in the propellant sample is not due to loss of molecular alignment. Examination of the birefringence changes in propellants prepared with 12.6 and with 12.2% nitrogen NC show the same similarity with the corresponding NC/NG paste fibre. The most reasonable interpretation of these observations is that when NC/NG paste is fully disintegrated to the molecular level no birefringence results, but the most persistant fibres, when finally gelatinized, do not disintegrate to the molecular level but to submicroscopic fibrils, the birefringence of which is the same as that of the macroscopic fibres. The loss of birefringence with increasing temperature in a polymer is sometimes regarded as a criterion of liquid crystal structure. Such an interpretation may not be valid in the present case.

CONCLUSIONS

(1) Birefringence measurement, and in particular its variation with temperature, has thrown light on a number of aspects of the structure of nitrocellulose fibres, nitrocellulose/nitroglycerine paste fibres, and propellants.

(2) Between $-100°C$ and $0°C$ nitrocellulose fibres undergo a series of reversible conformational changes, probably associated with the position of the primary nitrate group. The reversible loss of birefringence between $0°C$ and $130°C$ is also ascribed to increasing rotational freedom of the primary nitrate group.

(3) Birefringence changes produced by the sorption of nitroglycerine into nitrocellulose fibres become progressively less with increasing nitroglycerine concentration. At concentrations above about 50% w/w the system is effectively two-phase.

(4) Nitrocellulose/nitroglycerine paste fibres show irreversible annealing behaviour when heated to 130°C. The first heating curve from $-120°C$ to $0°C$ shows the same pattern as that of nitrocellulose itself, but at higher temperatures there is a much greater loss in the negative birefringence. Not only is much of this loss permanent, but the changes which occur at $-60°C$ in both nitrocellulose and in unannealed paste are no longer seen. This indicates that annealing is affecting the structure of the nitrocellulose itself and not just the plasticizer orientation.

(5) Residual nitrocellulose fibres in partially gelatinized propellant show a banded structure similar in appearance to certain lyotropic and thermotropic fibres which are frequently characterized as of liquid crystal structure. In the present case it appears that before final disintegration a highly plasticized fibre under the effect of shear forces takes on a pleated structure.

(6) The similarity in the birefringence of areas of apparently homogenixed propellant to that of the fibrous paste from which it was prepared suggests that dispersion is not to the molecular level but that a large number of discrete aligned sub-microscopic fibrils remain within the propellant.

ACKNOWLEDGEMENTS

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