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Effects of Electric Fields on Cholesterol Nonanoate Liquid Crystals

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Received December 9, 1965

Abstract—Effects of strong electric fields upon cholesteric liquid crystals have been studied. Increased intensity of light selectively scattered from the plane texture at d.c. and up to 3 kc have been found, as well as a temperature-dependent minimum in the average intensity as a function of frequency. An effect somewhat like hysteresis is shown by retention of the acquired brightness in the absence of field. Curious effects such as three classes of dark spots, some of which metamorphose into bars, light maltese crosses, and bright cross-hatchings are regularly observed.

These effects taken together with the conditions of their appearance imply strong alignment such that the selective reflection of the *cholesteric* mesophase is greatly enhanced by the increased ordering of the planes of reflection within the mosphase. The complicated a.c. electric field effects are given a detailed, qualitative explanation.

I. Introduction

This paper represents an extension of work reported in preliminary form elsewhere.¹ As pointed out by Ennulat,¹ the existence of an axis of symmetry of the optical scattering of the plane texture of the cholesteric mesophase implies an unique direction for the application of electric field. This direction is normal to the surfaces enclosing the plane texture.

This paper reports only on cholesterol nonanoate (hereafter CN). The effects of d.c. fields will be treated separately from those of alternating and transient fields.

II. Experimental

A chromatographically pure cholesteric liquid crystal was placed between an opaque and a transparent electrode, and visually examined by means of a polarizing trinocular microscope. The analyzer was crossed with the polarization of specularly reflected plane polarized vertical illumination. The electrodes were flat and normal to the viewing direction. Effects of various d.c. and a.c. electric fields, applied by means of the electrodes, were observed; both still and motion pictures were taken; and reflected light could be monitored by a photomultiplier. An oscilloscope was connected to the output of the photomultiplier to monitor rapid light changes. All light intensities quoted in this paper refer to a space average over a region of the sample containing of the order of ten or more elements of the largest visible structures.

Close control of the temperature was maintained throughout. The copper lower electrode was ground, lapped, polished, and heavily anodized; while the upper electrode was an 18 to 25 mm microscope cover glass with an evaporated film of either gold or indium sesquioxide. The latter was far more satisfactory as a transparent, conducting, and durable film. Alternatively, a 3 mm thick slab of conducting NESA glass was used for the upper electrode. Interferometric measurements indicate that the electrodes were within a few wavelengths of sodium light of flatness, the surface undulating gradually and smoothly with peaks being of the order of a millimeter apart.

The electrodes were spaced by a mylar washer of approximately 15 μ uniform thickness, which extended beyond the edges of the electrodes. A round hole of from 3 to 9 mm diameter was punched in this sheet, affording room for the sample. Thus, the cylindrical sample was bounded on the top and bottom by the electrodes and on the edges by the mylar. Unfortunately, because of the difficulty of getting the highly flexible mylar sheet absolutely flat and smooth and punching the hole without puckering the edges, it is impossible to be sure that the electrode spacing was less than 30 μ . To obviate these difficulties, improved apparatus is under construction. Capillary forces however, were quite large, holding the coverglass electrode firmly in place. Measurements were repeated with a washer cut with a slot connecting the center hole to the outer edge of the mylar to obviate hydrostatic effects.

The cholesterol nonanoate was chromatographically purified and checked.

III. Observations

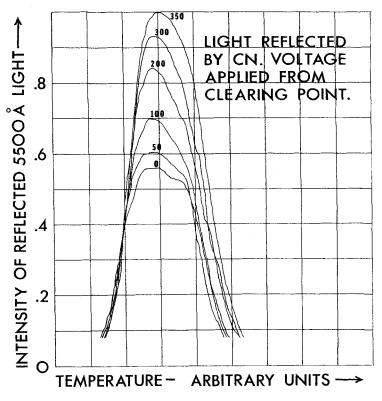
(A) D.C. FIELDS

The outstanding effect of an electric field is an increase in the intensity of selectively scattered light from the colored plane texture of the cholesteric mesophase. Although this is not ordinary specularly reflected light, we will, for convenience, refer to it as "reflected light". This reflected intensity is normally not merely a function of the present values of the temperature, mechanical deformation, incident light wavelength, and angles of incidence and reflection, but also of the past history of the temperature, and mechanical deformation. Along with these independent variables must now be grouped the present electric field and its past history. We have measured two cases, for which the mechanical deformation was negligible, the incident light wavelength fixed at 5500 Å, and the incident and reflected light approximately normal to the surface.

- (1) Intensity as a function of temperature, for different values of field applied above the clearing point, and maintained as the sample cools through the temperature range of selective reflection (hereafter "the color range"). It can be seen from Fig. 1 that the peak intensity is an approximately linear function of the voltage applied.
- (2) Intensity as a function of temperature, for different temperatures at which a field of constant magnitude was applied or removed, is shown in Fig. 2, together with two curves showing the effect of different thermal histories in the absence of field.

When the sample is cooled directly from above the clearing point with no field applied, the plane texture does not initiate in a mechanically undisturbed sample. If the sample is reheated from just below the color range, then the usual plane texture is initiated without field or mechanical displacement.

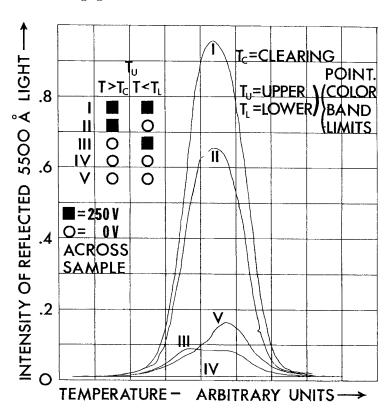
If the field is applied only within the color range to a sample that had been cooled undisturbed from above the clearing point, the plane texture is now induced, the reflected light in this case being the same as the usual scattering from the plane texture. However, if the field is applied at the clearing point and maintained until just above the color range and then shut off, as much as seven times greater reflection appears and remains. The greatest intensity



FIELD DEPENDENCE OF REFLECTED LIGHT FIGURE 1.

increase results from applying field continuously as the sample cools from above the clearing point down into the color range (see Fig. 2).

These observations taken together suggest a strong remanence of the optical behaviour of the liquid crystal with respect to these perturbing influences. The sample, however, cannot be brought to a state of zero reflection by cycling the field alone, since the reflected intensity is observed to be polarity independent; and forces maintaining alignment of the liquid crystal due to the walls of the sample cell are not negligible.



HYSTERESIS IN CN FIGURE 2

Qualitatively, it seems that an electric field applied normal to the plane texture does not alter the angle at which the peak intensity of a given color of scattered light occurs; but the angular distribution about the peak seems sharper.

All these observations, as well as those that follow, are reproducible not only on successive trials with the same sample, but also on different samples, and various electrodes.

In addition to these effects, there is an onset of small black spots for fields above approximately $1.5\times10^7~\rm V/m$. These spots are from 3 to $10~\mu$ diameter and suddenly appear and fade out in a somewhat

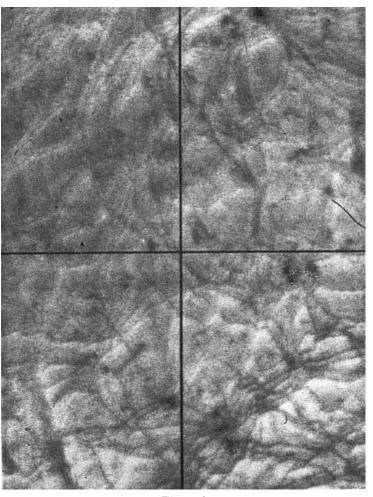


Figure 3.

irregular pulsation and random location (see Fig. 3). For this behavior there is a current density of the order of 10^{-7} A/cm² in the liquid crystal. Because these spots occur "Almost at breakdown", we designate them type "A".

Near 2.5×10^7 V/m dielectric breakdown of the liquid crystal takes place, with a visible spark and a pulse of charge, which is ballistically measured to be of the order of 10^{-5} C. The discharge is self-limiting; probably partly due to the very thin conduction layer on the upper electrode. This layer is burned off and open circuited over a small region around the discharge. Dielectric puncture of the mylar membrane has never been observed when there has been an alternate path of comparable length through the liquid crystal.

(B) A.C. AND TRANSIENT FIELDS

Because of the complex nature of the dynamic effects, several general remarks on the bare systematics of these observations will precede the detailed description of the phenomena.

- (1) The most characteristic a.c. behavior seems to be induced by the time rate of change of the field strength. To get the largest time derivative, most of the work was carried out with square waves. For a given peak value and period these have much greater time derivatives than sine waves. The peak value is limited by the need to avoid confusion between dielectric breakdown and other phenomena.
- (2) At lower temperatures, e.g., in the red part of the color range, as long as 15 min may be required to establish dynamic equilibrium after applying a.c. fields of between 1 and 10 cycles; while at higher temperatures, in the blue part of the color range, steady state is reached in a few seconds.
- (3) The sample history seems much less important for a.c. than for d.c. since almost any dynamic equilibrium state seemed attainable simply by waiting long enough at the final conditions.
- (4) Lastly, for a given type of behavior that occurs over a range of conditions, the change in frequency has the same sign as the change in temperature, if other factors remain constant.

Common to both a.c. and d.c. fields is an increase in reflected light.

For sinusoidal or square-wave a.c. the space average of the scattered light varies about an average value at twice the frequency of the applied a.c. field, and in phase with the absolute value of the field. For very low frequency square-wave a.c. fields there is a dip in intensity for each phase reversal. The dips are easily detectable up to an applied frequency of 1 kc. For square-wave pulsating d.c., the dips in intensity can be detected up to 3 kc.

At frequencies up to 1 c/s, approximately 10 μ diameter spots appear at each polarity reversal, and fade out between reversals during the constant portion of the square wave (see Fig. 4). Slightly less than half of the spots appear at the positive-going reversal; slightly less than half of the spots appear at the negative-going reversal; while the remainder, about 10%, appear at both changes of polarity. Thus most spots occur only once each cycle, while a few occur twice as often. Half of those appearing once each cycle are displaced 180% in phase from the other half. All of these spots are quite similar tothe type "A" spots and all occur at smaller fields of only about 1×10^7 V/m. Because of their "Bipolar" nature; all these spots are designated type "B". In the blue, the spots appear as light disks with Maltese crosses superposed (see Fig. 5). In the extreme blue and above the color band, up to the clearing point, the spots are bright rather than dark.

When such spots were produced by square-wave a.c. fields below 1 c/s, waves could be seen proceeding radially outward from each spot after every reversal, especially in the blue. These waves were confirmed by careful examination of motion pictures to be white rings spreading out from the spots and fading within about 15 μ radius.

As the frequency of the applied field increases, from 1 c/s, the spots grow in number until near 6 c/s in the red, and 12 c/s in the extreme blue, a maximum density is approached. There is then about 25 to 30 μ between spots, the spots being closer together and more numerous in the blue than in the red (see Figs. 4 and 5).

Near 8 c/s at the low temperature end of the color range, the spots grow very much larger, sending out fine dark lines toward each other, and then coalesce to form bars. These are very regularly

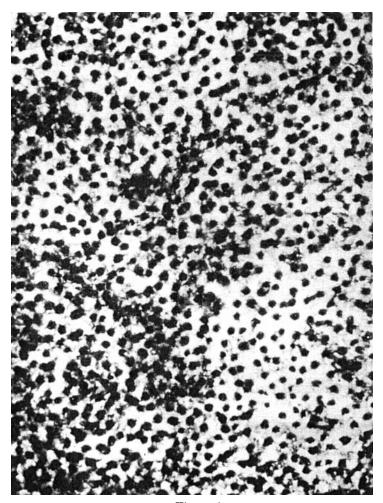


Figure 4.

spaced, approximately on 30 μ centers. The bars become again as narrow as 10 μ after coalescence. In some motion pictures taken at frame rates exactly double the frequency of the applied field, it is seen that physically alternate bars are shown on alternate motion picture frames. Of any two adjacent parallel bars, primarily only one will be visible in one frame, the other bar in the following frame,

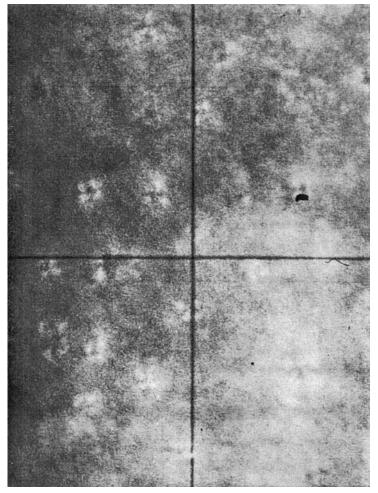


Figure 5.

and the first in the third frame, and so on. In the colored original to Fig. 6, the bars are very clearly seen to be alternate in appearance. This is the situation when the frame is unequally exposed for two phase reversals.

Long term equilibrium seems to favor bars ending normal both to free and to fixed boundaries of the fluid. In addition, there is a tendency for only even numbers of bars to end on topologically closed boundaries such as the bubbles in Fig. 6. Furthermore, though

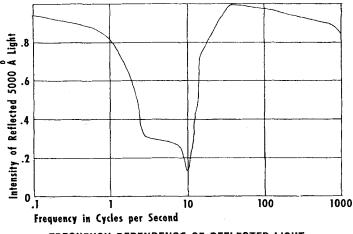


Figure 6.

we have observed closed rings, "Y" junctions and rudimentary double spirals in the bar pattern, no single spirals have been seen. The closed rings generally enclose other rings or a single bar.

To date, the bar pattern has been seen only in the red and orange part of the color range; for, if the temperature rises, the bars dissociate into spots.

As the frequency rises above 12 c/s, the bars start to fade, and are gone completely in the neighborhood of 25 c/s. For warmer samples (in the green and blue), the spots fade out without ever showing the bar phenomenon. Above the color range, the a.c. pattern takes on a cross hatched appearance which is quite similar to the pattern sometimes formed by battonettes. However, this pattern is far



FREQUENCY DEPENDENCE OF REFLECTED LIGHT Figure 7.

more blurred, lacking the sharp outlines that the battonettes possess. This pattern helps to define the clearing point by fading out very suddenly at that temperature, the contrast change being much larger than without the field. For the region above the color range, the spots fade out at higher frequencies—up to 30 cycles.

Measurement of the time average light intensity as a function of applied a.c. frequency are shown in Fig. 7. There is a broad minimum covering the range of spots and bars, and a narrow superposed minimum which coincides with the transition from spots to

bars. The high frequency reflectance is about the same as the very low frequency reflectance.

The last type of dark spot observed seems to be due to small dust particles which can be seen as such above the clearing point. A range of dust particle sizes is seen, varying from about 4 μ diameter down to totally unresolvable specks estimated to be of the order of 0.5 μ

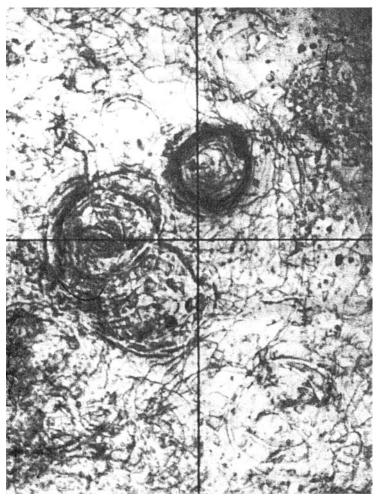


Figure 8.

in diameter. The behavior of all these dust particles is qualitatively similar, independent of size. Below the clearing point, the behavior of the dust is so distinctive as to warrant description, even though it is not an *inherent* property of the liquid crystal alone. Like the type "A" and "B" spots, the spots caused by dust are also about $10~\mu$ diameter. These spots also form Maltese crosses in the blue. However, much of the time the spots are in translation in almost circular paths at speeds of the order of $10~\mu/\text{sec}$. This motion is slow enough so that such a spot can be associated with a definite piece of dust above the clearing point. The orbits range in size from 15 to $75~\mu$ diameter. After a few trips around the same orbit, such a spot may be trapped for hundreds of revolutions. Or, the path may consist of a large number of highly irregular gyrations at very variable speeds. The spots frequently come to rest at some discontinuity, probably associated with an electrode surface.

Depending on the care used in preparing the sample, these spots vary in number from only several per slide, to as much as twenty-five. These therefore are far rarer for reasonably clean samples, than any other type of spot. These spots can always be distinguished from type "B" spots by the characteristic translational behavior, and by the existence of a moving center visible above the clearing point. Moreover, the dust spots continue in motion, after the frequency of the applied alternating current is so high that the type "B" spots have faded out. This is especially pronounced at the lower temperatures in the green and red regimes of the plane texture. Because of the existence of a "Center" to these spots they are designated type "C" (see Fig. 8).

IV. Discussion

In spite of the absence of certain desirable experimental evidence, a probable interpretation can be made.

The type "A" spots must represent some sort of pre-breakdown discharge which probably occurs at points of very high field. It is perhaps limited in its nature by the number of charge carriers separated per unit time on or near some surface anomaly. This charge could then build up locally in the fluid, while slowly neutraliz-

ing the dielectric polarization of the liquid near that spot, until the field internal to the liquid crystal exceeds breakdown. At this point, the discharge would cease very shortly; as the field would again be reduced after the removal of the charge. It should be emphasized that the above is primarily speculative and that further confirmation is lacking. In this connection, all the type "B" or "C" spots reported could be observed at fields 30 to 50% lower than for type "A" spots.

In what follows, we will suppose that there exist small ordered regions in the liquid crystal in which the molecules have definite average orientations. Whether such orientations are rigidly maintained or not, and whether such structures are continuously deformed from one point to another, or have no deformations until they come to definite boundaries, are questions of degree rather than kind.² No attempt will be made here to answer these questions, and such regions will be referred to as domains.

However, the very existence of an ordered fluid, stable at lower temperature than the disordered isotropic fluid, implies that a disordered region; whether inside, or outside, or at the edge of a domain; must have higher energy density than a structured region in the central portion of a domain. This excess energy density can be called domain wall energy. Thus, there is always an increase in the energy of the liquid crystal if it is too strongly broken up into small domains with large amounts of surface. This consideration is important because it helps limit the available possibilities among several dynamic modes to be discussed later.

Furthermore, we will assume that the optical properties of the ordinary plane texture differ from those of the bulk cholesteric liquid crystal due to an alignment imposed by the enclosing surfaces. It is postulated that the usual strong selective optical reflection is due to Bragg scattering from planes parallel to the exterior surfaces. The literature on these questions is summarized by Brown and Shaw³ and more recently by Gray.⁴

For cholesterol nonanoate a fundamental assumption is made here: that the d.c. electric field aligns the separate domains more completely to a common orientation than they are aligned by the exterior surfaces. In addition, the field may possibly improve alignment within a domain.

Because of the effect of the electric field on the liquid crystal, one has to postulate a permanent electric dipole moment for the cholesterol nonanoate molecules. This moment would be at fixed angles to the three axes of the molecules. Such profound effects as have been observed are not likely to be due only to an induced moment. Additionally, a gross dipole moment or charge separation in the fluid could not exist without molecular dipole moments or ionization. In this liquid crystal, ionization must be very small because of the very low leakage current observed. At the high fields employed, one would expect that even a low mobility could not prevent larger transport of charge than 1×10^{-7} A/cm². It is also expected on chemical grounds that the molecules could not easily dissociate into ion pairs. Moreover, the structure and atomic constitution of the molecule implies a dipole moment of the order of one Debye.

If the action of the electric field is sufficiently strong to produce alignment, then oriented regions of liquid crystal must possess sufficient dipole moment, and therefore sufficient field to experience considerable self-depolarizing fields. Such fields would usually limit the alignment near the surface of a domain and hence the size of domains in bulk samples. In the plane texture such considerations would be altered by the nature of the surfaces present. For example, a strongly polar insulating dielectric might produce strong local alignment by its exterior fields while a conductor might tend to neutralize self-depolarization fields. The increase in intensity produced by the electric field is therefore strong evidence that the liquid crystal is aligned by the electric field.

Moreover, the existence of Maltese crosses at the type "B" and "C" spots in the blue, is evidence for considerable local order around these centers. The visible features of the type "B" and "C" centers are produced only at the reversal of the field and fade out immediately afterwards. The appearance of these crosses is in fact, similar to that of uniaxial crystals between crossed polarizers in strongly divergent or convergent light. These centers occur only as

the result of an alternation from one state of electric polarization to the opposite. The fact that the centers are the same for dust particles (type "C" spots) as for the microscopically invisible centers of reversal of the "B" spots which are fixed in position relative to the electrodes, is very strong evidence that the spots are centered on a singularity where the reversal of alignment originates.

We suppose that those type "B" spots occurring twice each cycle are brought about by small conducting points or ridges which so greatly increase the field at each polarity of the applied voltage, that reorientation initiates at these points for both polarities. Though they comprise perhaps 10% of the spots near 1 c/s, they are no more than 1% of the spots at eight cycles, and their effect on the overall pattern of the bars is small.

On the grounds of the chemical structure of CN, the average direction of the permanent dipole moments of the molecules is supposed fixed relative to the molecular axes. Due to the flexibility of the molecule, the instantaneous dipole moment may be momentarily displaced from this direction. However, the number of molecules involved is so large as to render this displacement unimportant. Also the arrangement of the molecules even in such a highly ordered liquid crystal is probably well determined only in the time average. Therefore the reversal of alignment of the liquid crystal must be a physical reorientation of whole molecules. This is strongly supported by the observation of a low-velocity wave traveling outward from a spot at each appearance of the spot. The existence of this wave is also confirmed by the strong cooperation between adjacent spots, as the bars form.

First, the very regular spacing of the type "B" spots indicates a form of mutual exclusion. The coalescence of these into regularly spaced bars, effected by a small increase of applied frequency or decrease of temperature, indicates a particular type of cooperation preserving the proximity of each "spot" to a region of high reflectance.

Secondly, the alternate nature of the bars indicates two signs of the same phenomenon. This alternate nature is further strongly supported by the fact that physically adjacent bars or spots are alternate in phase or time, as discussed before. The evidence bearing on the above question shown by the pattern details of the bars is summarized as follows: (a) There are two types of bars; (b) These two types never merge continuously into one another; and (c) Each type is always laterally adjacent to the other type. We will hereafter refer to spots or bars initiated by opposite directions of field reversal as being of opposite sense or sign.

Third and last, the strong frequency dependence of the bar phenomenon shows a form of disturbance which must be transmitted from one bar to the next in exactly one half period. From the product of frequency and wavelength this velocity is about 0.5 mm/sec. The question that remains is what type of wave is involved.

The notion of reorientation suggests a torsional mode of oscillation, or a rotation. The forces driving the reorientation are assumed due to the interaction of the molecular dipole moments with the total electric field. This must be a superposition of the a.c. applied field, the field due to the dipole moments of the other molecules, and the static fields within the medium due to surface charges and dipoles on imperfections and insulating specks on the electrodes. These last contributions are reasonable because of the semiconducting copper oxide layer on the lower electrode, not to mention many possible types of surface contamination.

According to the direction and magnitude of such local fields there will be separate points of greatest reinforcement of the applied field for one polarity; and these will be different in general from those for the other polarity. Furthermore, these opposing polarities will tend to alternate in sign rather than accumulate, because of the discharge of many collected charges of one sign by the conductivity of the electrode.

Reorientation of the liquid crystal will originate near the points of high field, while around such points will be found strong lateral components to the field. The lateral components will tend to specify a sense of rotation to the reorientation. This sense will have circular symmetry around the point, having opposite signs on opposite sides of the point.

Thus there will be lines joining, and approximately perpendicular to, the electrodes along which lines the reorientation will originate as the instantaneous applied voltage increases after passing through zero during a reversal. Around these lines will be roughly doughnut-shaped regions in which the fluid will tend to reorient itself, after the center line does. In some ways the reorientation can be thought of as proceeding as the fluid flow in a vortex ring, the disturbance however, proceeding radially as in the luminous gas halo around a stellar nova. Due to the small mass and considerable viscosity, it is likely that the actual flow only involves a part of a revolution.

Because a reorientation wave traveling outward from one spot travels at a definite rate, the wave crest will be a definite distance away, after half a cycle, when the field reverses. A peak in the dielectric polarization in the liquid crystal will thus be in a ring around the original spot; but this polarization will be opposite to that induced by the now reversed field. Due to the fact that the dielectric polarization always creates an internal field opposing the field which produced the polarization; the total internal electric field in the liquid crystal will now be at a peak on the ring when the field reverses. Because of the great strength of the field on this ring, reorientation will initiate at the smallest anomaly near it. Thus spots of opposite sign will tend to be at definite distances apart.

Spots of the same sign can exist at lesser distances from each other than a half wave, but not very much closer together than the distance traveled by the wave during the rise time of the applied voltage reversal. This is because the induced polarization initiated by the reorientation at one spot will have an internal field canceling the applied field, thus reducing the total electric field at neighboring anomalies, before they might initiate reorientation.

In any event, there will be an interaction between any two such spots depending on the relative sense of the two. Those having the same sense will proceed approximately simultaneously, while those of opposite sense will be driven half a cycle apart in time. The increase in *number* of the spots as the frequency changes from 1 c/s up to 6 c/s must then be due to the shorter time between reversals

hence leaving less time for reorientation to propagate from a spot of one sign to the point where the opposite sign of spot initiates.

Spots of opposite sign will not be superposed because of the opposite preconditions for their initiation. Nevertheless, because of the limitation on accumulated local charge of one sign, it is most likely that spots of opposing sign will not be far apart. Furthermore, the competition between like kinds of spots and the definite rate of propagation of reorientation will lead to an equally densely packed situation for each sense of spot at frequencies between 6 and 8 c/s. (The frequency depends on the temperature.) In this situation, an alternation in signs of the spots is inevitable.

As the frequency approaches 8 c/s, the driving forces for reorientation will become sufficiently great to overcome the circular symmetry around the individual spots and it will become energetically favorable for the material to reorient in double rows of quasi-cylinders, rather than doughnuts. That is to say, the domain wall energy will become larger for the many closely packed doughnut configurations than for long rolls which have less surface where the disturbed medium must have a higher energy. What used to be the centers of the toroids will now occupy particular points along the centerlines between the long irregular cylinders, or rolls, whose axes will be parallel to the electrode surfaces.

From a dynamic viewpoint on the other hand, when the spots tend to come close together at high frequencies, the damped coupling of reorientation between adjacent regions around two spots of the same sign will increase because of the shrinking scale of events. This increased coupling, viscous and otherwise, will tend to disorder the overlapping regions between doughnuts of like sign, while reinforcing and unifying the regions between spots of opposite sign. Thus the regime associated with the areas between the spots of opposite sign will tend to grow at the expense of the areas between spots of like sign. Where the growing areas finally meet between the spots of like sign will be a sheet of singularity joining the centerlines of like spots and separating regions of opposite senses of reorientation. These sheets of singularity will appear as dark lines under the microscope where they are viewed from their edge.

In this connection, the bars tend to end normally on either free or fixed boundaries. Only where the fluid can flow in and out past a barrier are there appreciable numbers of bars parallel to the boundary. This strongly suggests that the wave energy is essentially propagated or exchanged perpendicular to the bars while it is primarily damped or reflected along the bars. The observed features exemplifying this coalescence of the spots are shown in Fig. 6, which shows a range of transitions due to a strong thermal gradient across the sample. It can be seen that dark lines join spots of like sign, while clear reflecting regions lie between spots of opposite sign.

One would, in general, expect the strongest normal mode of reorientation in a viscous medium such as a liquid crystal to be the physically largest possible rotational oscillation within the confining boundaries of the medium. The axis of rotation, of course, must be specified by the driving forces, and therefore limits the choice of modes. If the boundaries are two planes spaced about 15 μ apart, it would seem most likely that the oscillation would occur as partial rotation of long, narrow quasi-cylinders with long axes parallel to the planar electrodes; the cylinders being approximately 15 μ in diameter.

The torsional mode envisaged would reverse its rotation about the cylinder axis every half cycle of the applied electric field, while the distance between two adjacent bars would be a half wavelength of the reorientation wave.

Unfortunately, there is an implicit contradiction in the experimental evidence for the phenomenon; namely, that the spacing between the bars is definitely near 30 μ and therefore is about twice as great as the supposed space between the electrodes. For such a cross-section, an outright rotational mode would be very much hindered by the boundaries. Two explanations are possible: (a) The mode of oscillation is not correctly identified; and (b) The spacing is not as small as the thickness of the mylar washer, due to the wrinkles in the washer between the electrodes. This certainly is the case in Fig. 6, as can be ascertained from the motion picture from which it was taken. In fact, there is considerable fluid flow

over the washer wherever the bars are not normal to the boundary of the layer of mylar. (The large gentle arc in one corner of the picture.) Whether this is enough of an error to rule out the misidentification of the mode on these grounds is uncertain.

It is therefore only tentatively concluded that the nature of the oscillations induced in the liquid crystal is correctly set forth above. It must be strongly emphasized that the theory presented is at best tentative, and awaits more definitive experimental data.

Acknowledgments

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REFERENCES

- 1. Muller, John H., Z. Naturf. 20a, 849 (1965).
- 2. Furth, R. and Sitte, K., Ann. Phys. 30, 388 (1937).
- 3. Brown, Glenn H. and Shaw, Wilfrid G., Chem. Rev. 57, 1071 (1957).
- Gray, George W., Molecular Structure and Properties of Liquid Crystals, p. 44, Academic Press, New York (1962).