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Mechanism of Surface Alignment in Nematic Liquid Crystals†

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Abstract—Chatelain hypothesized that orientation of liquid crystals by interaction with the substrate is due to an adsorbed layer of fatty contaminants, but substrate topography has also been postulated as a causal factor. Experiments with chemically cleaned surfaces rubbed without contamination now confirm the importance of the impurity layer, which has been investigated using Auger spectrometry. Through the use of known surfactants, intentionally deformed substrates, and electron microscopy, the roles of surface topography and surface chemistry have been distinguished: substrates with surface energy lower than the liquid crystal surface tension cause homeotropic alignment; otherwise alignment is parallel to the substrate plane, following any long-range order, e.g., grooves, present on the surface.

Early in liquid crystal research, observations were made concerning the spontaneous interaction of the fluid with surfaces.(1) Chatelain,(2) in his classic investigation of homogeneous alignment on rubbed surfaces, hypothesized that orientation results from dipole interactions between an ordered layer of adsorbed fatty impurities and the proximate nematic molecules, but he was unable to eliminate the possibility that the mechanism involved alteration of the substrate surface itself. Recently, Berreman(3) gave a rationale for the latter type of mechanism. The purpose of this paper is to investigate the roles played by the chemical nature of the surface and by surface topography in liquid crystal alignment.

Because of observations that the cleanliness of the substrate is involved in liquid crystal behavior, it is essential for the study of surface alignment to employ a cleaning procedure which repeatably produces a uniform and reproducible chemical surface, particularly

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one which is free from organic contaminants. Likewise the efficacy of cleaning procedures must be constantly checked by an appropriate monitoring technique and by carrying cleaned untreated controls through all experiments. A discussion of the cleaning and monitoring procedures used in the present work will precede the results of the study itself.

1. Cleaning and Determination of Cleanliness

The art of cleaning consists of removing undesired materials. These contaminants can be divided into inorganic and organic residues with the latter class playing the major role in initial surface alignment of liquid crystals. An extensive evaluation of cleaning processes was performed by Feder and Koontz.(4) Tests based on the surface tension of water were used to compare the efficacy of the cleaning methods studied. They found that many widely accepted cleaning methods do not remove the last few monolayers of organic contaminants. Even heat treatments which are commonly thought to completely remove organic materials only tend to convert residues to tars which may be quite resistant to oxidation.

Although the work by Feder and Koontz was performed on nickel sheet, others(5) have obtained similar results on glass and sapphire. Their conclusions indicate that detergents, solvents, and non-oxidative heat treatments are relatively ineffective in freeing high energy surfaces from organic residues. Strongly oxidizing conditions are necessary to remove organic contaminants, and preservation of a clean surface is difficult. Consequently it is best to clean substrates shortly prior to test and to monitor cleanliness frequently.

The determination of the degree of cleanliness obtained by a given process is not simple. Feder and Koontz(4) suggest using an atomizer (fog) test in conjunction with freshly cleaned mica as a process monitor. Properly performed,(6) this type of test can detect a tenth of a monolayer of organic material, making it several times more sensitive than the water break test. In addition we have used Auger spectroscopy, which indicates the elemental composition of any residues. This technique, like most display applications, requires a conducting substrate: tin oxide-coated (NESA) glass was adopted as the standard substrate throughout this work because it can be cleaned much more stringently than indium oxide-coated glass.

Figure 1 illustrates the type of data that is obtained by Auger spectroscopy. On tin oxide cleaned so as to have no carbon peak in the spectrum, MBBA and various other liquid crystals tend to align homeotropically; however if the cleaning is imperfect and a peak for carbon indicates organic contamination as shown in the second trace, then 4′-methoxybenzylidene-4-butylaniline (MBBA), 4′-ethoxybenzylidene-4-cyananiline (PEBAB), and *p*-azoxyanisole (PAA) tend to align parallel to the plane of the substrate. The samples represented by Fig. 1 were indistinguishable by water break tests.

Results obtained with several cleaning procedures are compared in Table 1. Note that residual metal ion contamination, commonly expected with acid cleaning, was absent in properly rinsed samples. The cleaning method chosen for this work is a hot chromic acid wash followed by rinsing in flowing filtered deionized water for a minimum of one hour prior to drying in nitrogen.

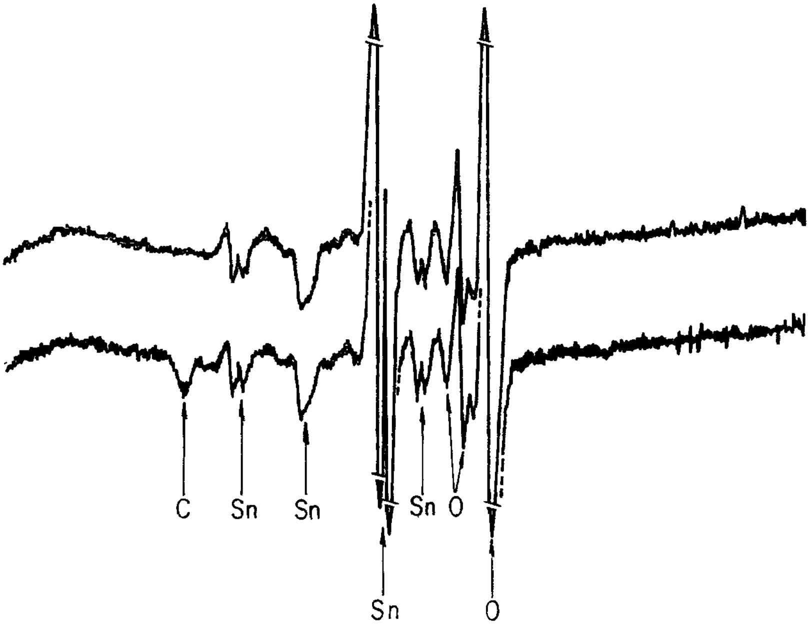

Figure 1. Auger spectra for tin oxide. Top trace: Sample cleaned in hot chromic acid and rinsed in flowing deionized water. Bottom trace: Sample cleaned in commercial sulfonic acid cleaner and rinsed in flowing deionized water.

TABLE 1 Auger Intensity Ratio of Element to Tin

Type of Clean-Up	Element O	 C	 Cl	 Fe	Results of Atomizer Test	 Water Break Test
Chromic Acid	0.66	0.093	0	0	Passed	Passed
HNO_3/H_2SO_4	0.64	0.096	0	0	Passed	Passed
Sulfonic Acid	0.64	0.13	0	0	Failed	Passed
Alconox	0.80	0.36	0.086	0.019	Failed	Failed

2. Surface Alignment Experiments

To distinguish between the effects of surface topography and the chemical nature of the surface on the alignment of liquid crystals, the series of experiments represented by the matrix in Fig. 2 was performed. The results shown summarize the behavior of MBBA(7) on tin oxide. Similar results were obtained with other nematic materials including PEBAB, Licristal IV and V, and PAA.

On rigorously cleaned substrates, MBBA tends to form a homeotropic layer after an initial period in which orientation of the long axes of the molecules is parallel to the surface. The duration of this transitory random homogeneous alignment decreases as the filling temperature is increased above ambient. The presence of small percentages of the starting materials *p*-*n*-butylaniline and *p*-anisaldehyde reduces the tendency to homeotropic alignment as shown by an increase in the alignment transition time from a few hundred milliseconds to seconds.

Surfactant Grooves	None	Lecithin	Carbon
No	⊥ (Random tilt with E)	⊥	Random ∥
Yes	⊥ (Tilt along grooves with E)	⊥	∥ Homogeneous

Figure 2. Alignment of MBBA with SnO_2/glass substrate.

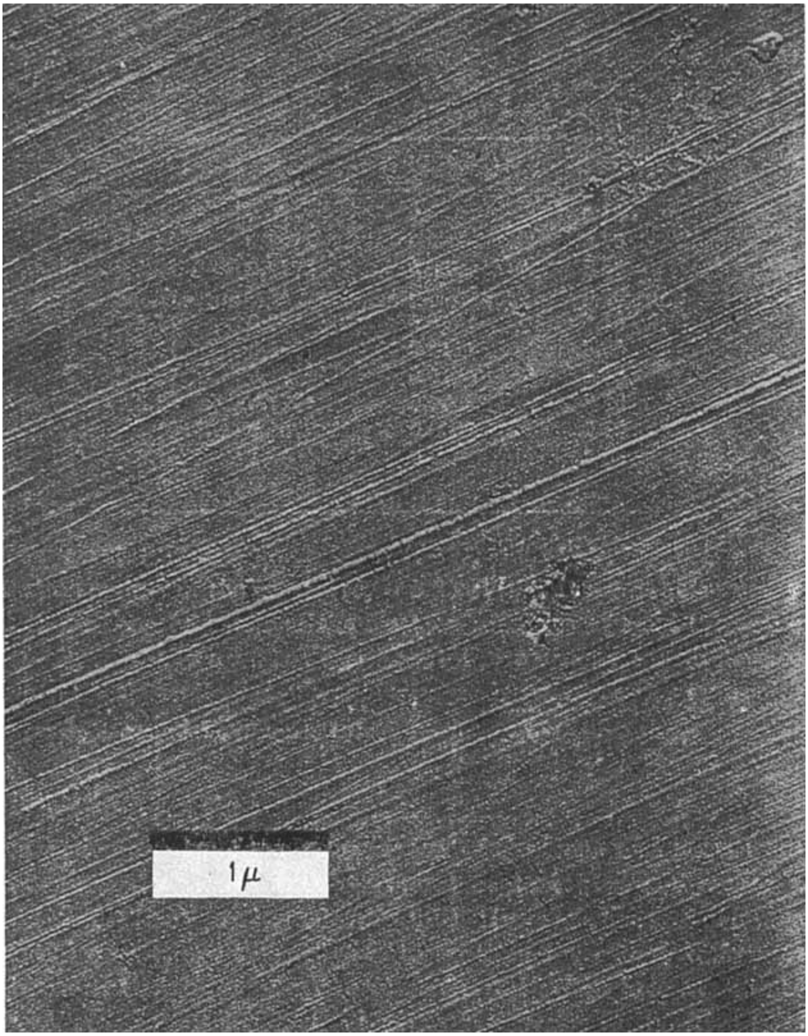

Figure 3. Scanning electromicrograph of deformed substrate: Glass grooved with 1μ diamond paste, then cleaned.

To alter substrate topography, samples were rubbed with a diamond abrasive slurry. Figure 3 is typical of scanning electron micrographs taken after cleaning. They confirm that the normally smooth surface has been grooved. Rubbing with various cloths and papers produced no discernible surface deformation. In all cases,

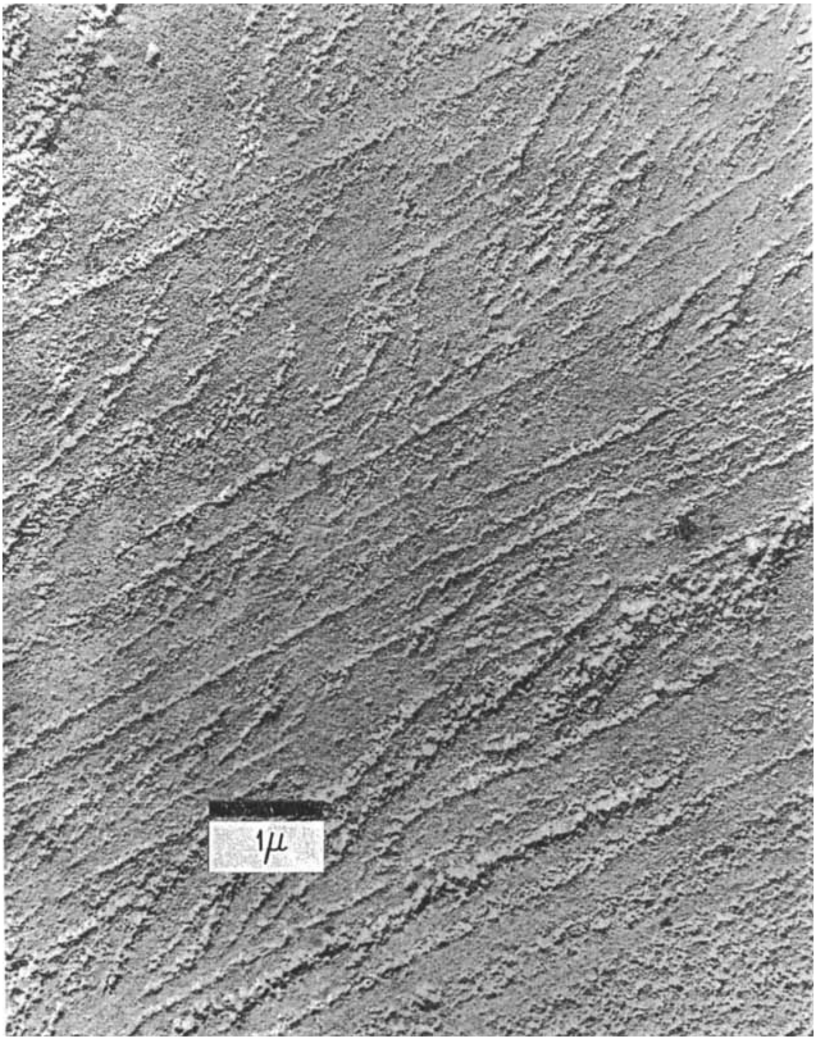

Figure 4. Transmission electron micrograph of a platinum–paladium shadowed carbon replica of a rubbed lecithin surface.

homeotropic alignment was again obtained as long as the substrates regardless of topography, were clean.

3. Substrate Chemistry

When clean substrates were coated with a known surfactant such as lecithin or carbon, the choice of orientation perpendicular or parallel to the plane of the substrate was likewise independent of the topography, being determined by the chemical nature of the surfactant. Figure 4 is a transmission electron micrograph of a platinum–paladium shadowed carbon replica of a grooved lecithin surface. This observation technique was used to prevent destruction of the organic surface layer by direct electron bombardment. Despite the grooves, the surface produced homeotropic alignment. On the contrary, grooved or smooth surfaces of carbon produced alignment parallel to the substrate plane.

That specific chemical interactions are necessary to determine alignment is also shown by Proust and Guyon.(8) They carefully deposited hexadecyltrimethylammonium bromide in oriented monolayers so that in one case there was close molecular packing to establish a methyl surface(9) and in the other a more diffuse film in which the surfactant molecules were lying parallel to the glass surface. MBBA was found to give homeotropic alignment on the dense methyl layer and parallel orientation on the other. It is significant that the surface energy presented to the liquid crystal is lower in the case of a methyl surface than a methylene–carbonyl surface.(9)

A prediction of the orientation that liquid crystals will assume on a given surface can be made based on the relative magnitudes of the surface energy of the substrate and the surface tension of the liquid crystal. When the substrate surface energy is relatively low, the intermolecular forces within the liquid crystal are stronger than the forces across the interface. The fluid does not wet the solid, and the elongated nematogenic molecules align perpendicular to the surface to maximize their intermolecular interactions.(10) This is the same alignment as has been observed, for example with MBBA,(11) at a free liquid surface. When the critical surface tension of the solid is greater than that of the liquid crystal, the forces across the interface dominate. Then surface energy is minimized if the fluid wets the solid and the elongated liquid crystal molecules pack flat against the substrate.

Measurements of the surface energy of several substrates, obtained by the contact angle method, are compared in Fig. 5 with the surface tension of MBBA which is determined by the platinum ring technique

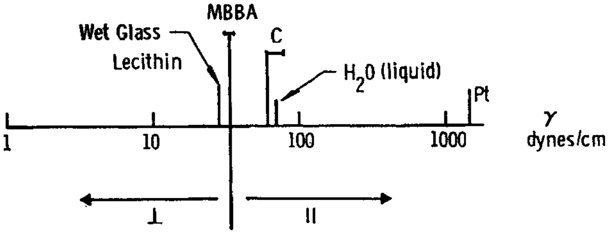

Figure 5. Alignment of MBBA on substrates of various surface tensions.

to be 32–34 dynes/cm at 25 °C.(16) Lecithin is an example of surfaces with energy lower than MBBA: liquid crystal alignment is perpendicular to such surfaces. Alignment is parallel to the substrate on carbon coatings whose surface energy is higher than MBBA.

The observation of perpendicular alignment on clean glass to which a very high surface energy is commonly attributed does not fit this model and requires explanation. Shafrin and Zisman(12) have shown that the effects of adsorbed water on the surface tension are so great that even at 0.6% relative humidity, glass has a critical surface tension of only 45 dynes/cm; at ordinary relative humidities the surface tension is about 30 dynes/cm at 20 °C. They found an outer layer of physically adsorbed water to be readily removed but there remains chemically adsorbed water that is removed only by vigorous and prolonged heating. Exposure to even low levels of moisture results in a water saturated surface. With MBBA, adsorbed hydrolysis products can further alter the effective surface energy.

To eliminate these effects of adsorbed moisture, one substrate in an MBBA sandwich cell was partially covered by flame-cleaned platinum foil. This region assumed random parallel alignment while the usual homeotropic alignment prevailed where both substrates in contact with the liquid crystal were glass. The alignment on the water-free platinum thus agreed with the prediction for high energy surfaces. Janning(13) likewise reports homogeneous alignment on freshly evaporated metals and metal oxides, which have high surface energies.

4. Substrate Topography

The effect of grooving the substrate is also indicated by the experiment matrix of Fig. 2. Smooth samples coated with carbon produce a "speckled" orientation pattern with alignment generally in the substrate plane but with extinction directions varying from one small region to another. Grooved carbon samples give homogeneous orientation parallel to the grooves. This effect can also be observed in the homeotropic samples through the Freedericksz transition in an electric field.(14) Initially homeotropic MBBA molecules between smooth lecithin-coated electrodes tilt away from an electric field in a disorganized manner, but they all tilt toward the grooving direction on grooved lecithin.

In the conventional Chatelain technique for production of homogeneous alignment, samples are rubbed with cloth or paper without the intentional application of any surfactant.(2) However Auger spectroscopy reveals that organic contamination of initially clean samples occurs during the rubbing process unless the most stringent precautions are taken in handling. Furthermore, replica electron microscopy shows that this unintentional surfactant layer is grooved like the lecithin in Fig. 4. Through the use of disposable plastic gloves, freshly cleaned tools, glassware and materials, and great care, we have succeeded in rubbing clean substrates without introducing detectable contamination: homeotropic alignment without evidence of grooving was obtained.

It is evident that the conventional rubbing technique produces homogeneous alignment by grooving a fortuitous organic surface layer. In view of the difficulty of rubbing without chemically contaminating the surface, deposition of a known surfactant layer to conform to a previously grooved clean substrate was found to be more reliable for the purposes of the present study than rubbing a smooth surfactant layer to produce grooves.

The grooves evidently provide a preferred direction for long-range order in the plane of the substrate. When either the high surface energy of the substrate or an applied field constrain the nematic molecules to lie parallel to the substrate, the elastic energy of the liquid crystal is clearly lower if the director is parallel to the grooves instead of following the curvature of the substrate deformations. This contribution to elastic energy has been calculated by Berreman(3) and by Grabmeier *et al.*(15)

5. Conclusion

In summary, quiescent alignment is determined by the interaction of the liquid crystal with the substrate, clean or treated with a surfactant. On low energy substrates, alignment is homeotropic. If the substrate is of the proper chemical nature to give high surface energy and is unordered, orientation is locally homogeneous. If a high surface energy substrate possesses long range order, then the liquid crystal will assume uniform homogeneous alignment. For example, the long axes of nematic molecules will lie parallel to the direction of grooves in a rubbed substrate.

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REFERENCES

1. For example: Freedericksz, V. and Zolina, V., *Trans. Far. Soc.* **29**, 917 (1933); Friedel, G., *Ann. Physique* **18**, 273 (1922).
2. Chatelain, P., *Bull Soc. franc Miner. Crist.* **66**, 105 (1943).
3. Berreman, D., *Phys. Rev. Letters.* **28**, 1683 (1972).
4. Feder, D. O. and Koontz, D. E., Bell Telephone System Technical Monograph 3143, 1959, p. 33.
5. Fox, H. W., Hare, E. F. and Zisman, W. A., *J. Am. Chem. Soc.* **59**, 1097 (1955), and related papers.
6. ASTM Bulletin ISO May 1953, p. 47 (TP43).
7. Purity of MBBA was determined by gas chromatography: Samples used were 99.99% MBBA unless otherwise noted.
8. Proust, J. E., Ter-Minassian-Saraga, L., and Guyon, E., Sol. St. Commun **11**, 1217, (1972).
9. Fox, H. W., Hare, E. F. and Zisman, W. A., *J. Colloid Soc.* **8**, 194 (1953).
10. de Boer, J. N., *The Dynamical Character of Adsorption*, Oxford 1968, 2nd Edition, p. 150–153.
11. Bouchiat, M. A. and Langevin-Cruchow, D., *Phys. Letters* **34A**, 331 (1971).
12. Shafrin, E. G. and Zisman, W. A., *J. Am. Ceramic Soc.* **50**, 478 (1967).
13. Janning, J. L., *Appl. Phys. Letters* **21**, 173 (1972).
14. Kahn, F., *Appl. Phys. Letters* **20**, 199 (1972).
15. Grabmaier, J. G., Greubel, W. F., Kruger, H. H. and Wolff, U. W., Paper 103, presented at Fourth International Liquid Crystal Conference, Kent, Ohio, August 1972.
16. When normalized by the Harkins and Jordan correction factor, this value is in good agreement with the more precise measurement of 28.8 ±0.03 dynes/cm reported recently by Kahn, F. J., Taylor, G. N., and Schonhorn, N., *Proc. IEEE* **61**, 823 (1973).