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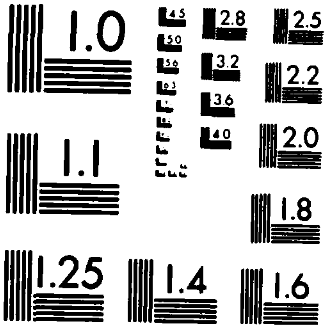

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IMPROVED MATERIALS FOR DC DYNAMIC SCATTERING AT ELEVATED TEMPERATURES

by

Anna M. Lackner and J. David Margerum

To Be Presented at the Tenth International Liquid Crystal Conference,
York, U.K., July 15-21, 1984

Hughes Research Laboratories
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to the level of contamination they introduce at elevated temperature. One UV-curved sealant shows no apparent degradation effects after more than 1800 hours of 100°C heating with an undoped ester LC in a vacuum-filled test cell made with this sealant. Thermal storage stability at 80°C and low temperature stability at -60°C in such sealed cells show little change in surface alignment, resistivity, and DS characteristics in LCs with redox dopants; namely, dialkylferrocene and (2, 4, 7-trinitro-9-fluorenylidene)-malononitrile. The LC materials with this redox dopant also show good thermal stability for over 1100 hours at 100°C in evacuated glass ampoules. Elevated temperature dc-DS stability with 20 V dc at 55°C shows more than 5000 hours for two of the new redox-doped LC mixtures in sealed transparent cells. The viscosity, dielectric anisotropy, conductivity anisotropy and dc-activated DS effects are studied as a function of temperature for one of the mixtures. Response times of DS as a function of temperature (25°C to 65°C) and cell thickness are also studied.

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IMPROVED MATERIALS FOR DC DYNAMIC SCATTERING AT ELEVATED TEMPERATURES*

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Liquid crystal (LC) mixtures and a sealant suitable for dc-activated dynamic scattering (DS) matrix displays are developed for wide range storage temperature (-60 to 80°C) and for elevated temperature operation. Three improved eutectic nematic mixtures are formulated with nematic ranges (undoped) of 0 to 74, -4 to 82, and -13 to 78°C, with flow viscosities of 31, 32 and 36 cP respectively. Several types of sealants are tested in contact with LC and are evaluated according to the level of contamination they introduce at elevated temperature. One UV-curved sealant shows no apparent degradation effects after more than 1800 hours of 100°C heating with an undoped ester LC in a vacuum-filled test cell made with this sealant. Thermal storage stability at 80°C and low temperature stability at -60°C in such sealed cells show little change in surface alignment, resistivity, and DS characteristics in LCs with redox dopants, namely dialkylferrocene and (2,4,7-trinitro-9-fluorenylidene)malononitrile. The LC materials with this redox dopant also show good thermal stability for over 1100 hours at 100°C in evacuated glass ampoules. Elevated temperature dc-DS stability with 20 V dc at 55°C shows more than 5000 hours for two of the new redox-doped LC mixtures in sealed transparent cells. The viscosity, dielectric anisotropy, conductivity anisotropy, and dc-activated DS effects are studied as a function of

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1. INTRODUCTION

The dynamic scattering (DS) mode is useful for several types of liquid crystal (LC) display applications[1], most of which require a wide temperature range for device storage as well as a fairly wide operational temperature range for the LC materials. However, because the DS mode is dependent upon the anisotropic conduction of ionic species, the operational range is in general somewhat limited due to the exponential dependence of ionic conduction upon temperature. We are particularly interested in using dc-activated DS for an active-matrix pictorial LC display with MOS (metal-oxide-semiconductor) substrate circuitry[2-5]. The dc-DS mode provides a gray scale capability for this matrix display, and dc-activation of the LC picture elements (pixels) is the simplest way to utilize the MOS circuitry. In this circuitry a field effect transistor (FET) is switched open just long enough to charge a pixel capacitor, which provides the activating voltage across the LC pixel during each picture frame time (e.g., 33 ms). The LC must be conductive enough to give a full level dc-DS response, but must be resistive enough so that the capacitor remains sufficiently charged to maintain an adequate voltage across the LC during the frame time. At room temperature with a typical LC thickness (e.g., 10 μm) the operational range for the LC resistivity in this MOSFET addressed display is approximately between 10^9 and 10^{10} ohm-cm. The resistivity is strongly temperature dependent for redox doped LC esters[1], with an order of magnitude change between about 25 and 70°C for the ac-resistivity and between about 35 and 71°C for the apparent dc-resistivity for cells activated at 20V.

Although the use of redox dopants[6] permits long lifetimes for the dc-activation of ester LCs, the resistivity of unsealed cells gradually increases over long periods of dc operation, even in nitrogen-flushed ovens.[1,6] On the other hand, cells sealed with epoxy type sealants have shown a very short dc-lifetime at elevated temperatures due to electrochemical effects from ionic impurities introduced into the LC from the sealant material.[1] The present work was initiated with the goal of obtaining improved LCs and sealants compatible with the dc-activation of MOS-addressed matrix displays in the elevated temperature range of about 35 to 71°C. Cells can be readily heated, and operation above room temperature is advantageous for faster response times. In addition, environmental conditions may require operation up to about 71°C in some cases if the cells are not cooled. Our aims were (1) to develop improved redox-doped ester LC mixtures with a wider nematic temperature range, lower viscosity, and faster response times, and (2) to obtain sealants compatible with these LCs and capable of permitting long life dc-activation of MOS-addressed matrix cells at elevated temperatures as well as long term storage at both high and low temperatures.

2. EXPERIMENTAL

The LC components used in these studies belong to the structural classes shown in Figure 1. The class code nomenclature is similar to ones we have used previously.[1,7-11] For specific compounds the R and R' end groups are identified numerically by the number of carbon atoms in their n-alkyl end groups, e.g., 20-3 refers to p-ethoxyphenyl p-n-propylbenzoate. The synthesis or source of the individual compounds is given in the Figure 1 references. The LC purity and properties are measured as described previously.[1,7-10] For DS studies "redox dopants" were added, generally 0.5% each of a dialkylferrocene and (2,4,7-trinitro-9-fluorenylidene)malononitrile (TFM). Either dibutylferrocene (DBF) or dihexylferrocene (DHF) are used. The DBF is used in HRL-26N4 and -26N25, and the DHF in HRL-26N35 and -26N36. The TFM and DBF were purified commercial products, while the DHF was synthesized by acylation of ferrocene with hexanoyl chloride to give dihexanoylferrocene, which was then reduced to DHF and purified. The DS measurements are made in the same manner as before,[1,7,8,12] namely in transmission at normal

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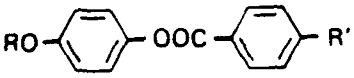
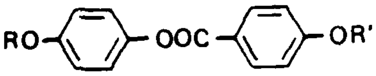
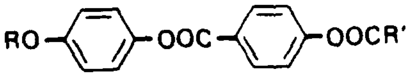
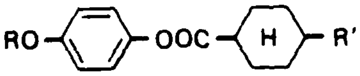
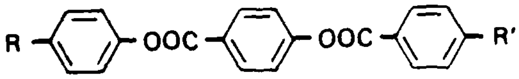
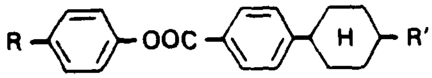
	RO–R′	1, 7
	RO–OR′	1, 9
	RO–OOCR′	1, 9
	RO–[C] R′	1, 8
	R–OOCPR′	9, 10
	R–OOCYR′	10, 11
	R–YR′	10

FIGURE 1 Structure and code symbols for classes of LC ester components used in these studies.

incidence using unpolarized, collimated green light centered at 525 nm, with a detector acceptance angle of about ±2°. The DS response times are measured in unsealed cells made from optical flats with several hard SiO$_x$ spacer pads deposited near the perimeter. The thickness of these empty cells are measured by a standard interferometer technique with a Cary 14 spectrophotometer. The LC in both sealed and unsealed cells are surface-parallel aligned, by rubbing the spin coated and oven-baked polyvinyl alcohol (PVA), as before,[1] on indium-tin oxide (ITO) transparent electrodes on float glass. The LC ac-resistivity is normally measured at 100Hz with 0.1V rms in cells with surface-parallel alignment, although some nominal dc-resistivity values are shown at 55°C and 20V dc while the LC is undergoing DS. The materials used for sealing tests are identified by their manufacturer's code, and the sealing (curing) conditions are those recommended by these suppliers.

3. RESULTS AND DISCUSSION

3.1 New LC Mixtures: Composition and Properties

The compositions of the three new ester mixtures HRL-26N25, -26N35, and -26N36 are given in Table I along with that of HRL-26N4. The latter is shown for comparison purposes, since it was one of the better mixtures that we studied previously for use at elevated temperatures.[1] The techniques of formulating these new mixtures were described recently:[10] The components were selected to give mixtures with a wider nematic range (especially a lower melting point), a lower viscosity, and a

TABLE I. Composition of Liquid Crystal Eutectic Mixtures.

Component	Mole Fraction of Components in HRL Mixtures			
Component Code	26N4	26N25	26N35	26N36
20-3	0.108	0.061	0.054	0.057
20-5	0.120	0.057	0.058	0.062
40-1	-----	-----	0.037	0.039
40-3	-----	-----	0.034	0.036
40-6	-----	-----	-----	0.110
60-5	-----	0.229	0.204	0.214
60-01	0.194	-----	-----	-----
10-00C3	0.058	0.037	0.032	-----
40-00C4	0.073	0.045	-----	-----
60-00C5	0.223	-----	-----	-----
10-[C]5	-----	0.272	0.245	0.256
20-[C]3	0.222	0.142	0.124	-----
20-[C]5	-----	0.077	0.066	0.070
4-00CY4	-----	-----	0.059	-----
4-00CP4	-----	0.070	-----	0.065
3-Y3	-----	-----	0.087	0.091

less negative dielectric anisotropy than HRL-26N4. These changes were accomplished primarily by replacing the RO-OR' component and one or more of the RO-OOCR' components with more structures containing cyclohexyl groups, such as RO-⌊C⌋R', R-YR', and R-OOCYR'. The resultant properties of the undoped mixtures are shown in Table II, and these are in fairly good agreement with the calculated values predicted[10] for melting point, clearpoint, birefringence (Δn), viscosity (η), and dielectric anisotropy ($\Delta\varepsilon$). The conductivity anisotropy ($\sigma_{\parallel}/\sigma_{\perp}$) was measured after doping the mixtures with 0.5% each of a dialkylferrocene and TFM, and then filtering the LC to remove any undissolved particles. Typical dc-DS curves of percent scattering (%S) versus voltage are shown in Figure 2 for these four mixtures. The HRL-26N36 mixture has the best scattering characteristics of the three new mixtures, and it is the one most comparable to HRL-26N4. The superimposition of a high frequency bias signal (5 or 10V of 10kHz) shifted the dc-DS curves of HRL-26N36 considerably toward higher threshold voltages and steeper %S changes just above threshold. However, these high frequency bias signals had a small effect on the DS response times at 20V dc; for example, a cell of 11.3 μm thickness showed on-times of 18, 26, and 25 ms and decay times of 132, 140 and 123 ms respectively for 10 kHz bias voltages of 0, 5, and 10 V rms.

3.2 Elevated Temperature Effects on LC Properties

The data in Figures 3, 4, and 5 show the effects of elevated temperature on several important LC properties, comparing HRL-26N36 with HRL-26N4.

TABLE II. Properties of LC Mixtures

Property[a]	Mixture HRL Number			
	26N4	26N25	26N35	26N36
Melting Point, °C	21	0	-4	-13
Clearpoint, °C	77.0	73.9	81.9	77.6
Average Length, Å	23.3	23.2	23.0	23.8
Δn at 23°C	0.14	0.12	0.12	0.13
η at 25°C, cP	49	31	32	36
$\Delta\varepsilon$ at 25°C[a]	-0.96	-0.57	-0.70	-0.28
$\varepsilon_\perp$ at 25°C[a]	6.15	5.04	4.85	4.84
$\sigma_\parallel/\sigma_\perp$ at 25°[b]	1.40	1.44	1.56	1.42

[a] Measured at 500 Hz

[b] Measured at 100 Hz with 0.5% redox dopant

The temperature effect on the ac-resistivity ($\rho_\perp$) of the redox-doped mixtures is similar to the temperature effect on the flow viscosity of the undoped mixtures, as illustrated by the $\rho_\perp$ and η comparisons shown in Figure 3. Both viscosity and resistivity show a similar exponential dependence on T^{-1}, with their log plots showing similar deviation from linearity at higher temperatures. The effect of temperature on the conductivity anisotropy of redox-doped HRL-26N36 is similar to

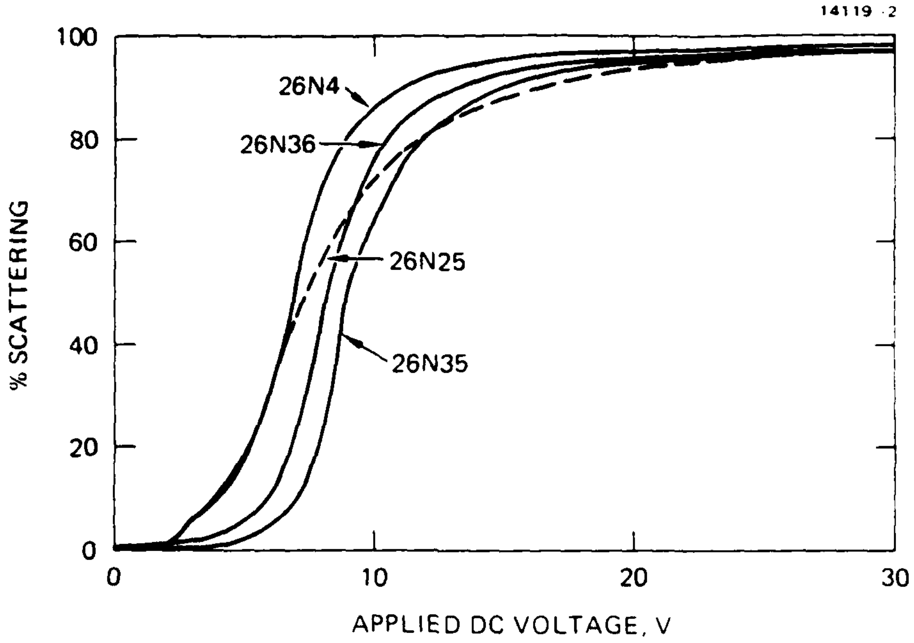


FIGURE 2 DS curves, 12 μm thick cells of optical flats/ITO/PVA (rubbed), 23°C.

that of HRL-26N4, as shown by the comparisons in Figure 4. The $\sigma_{\parallel}/\sigma_{\perp}$ of HRL-26N36 is higher at all temperatures, and it is above 1.3 even at 70°C due to the relatively high clearpoint of this mixture. The temperature effects on the dielectric anisotropy and dielectric constant of these two mixtures are compared in Figure 5. As indicated in Table II, the Δε values for HRL-26N25 and -26N35 are intermediate between those of HRL-26N4 and -26N36.

Temperature and cell thickness effects on the scattering versus voltage curves for the dc-DS of

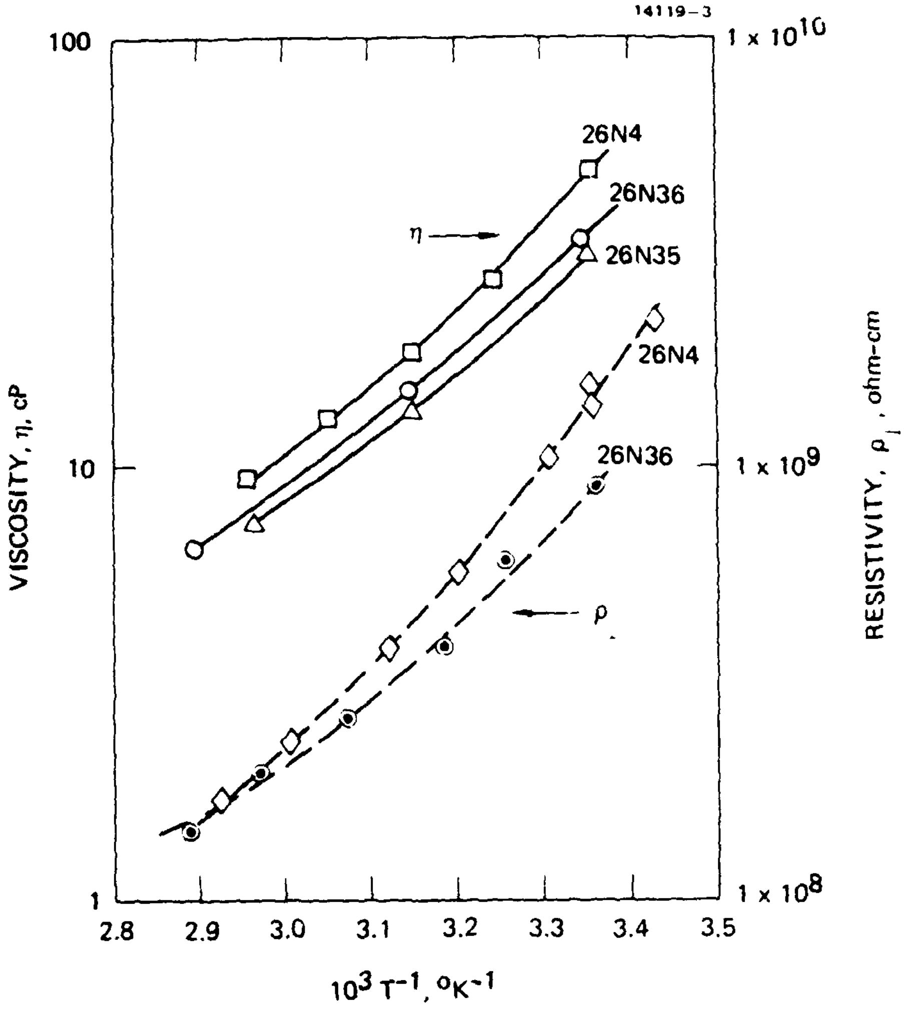


FIGURE 3 Effect of temperature on flow viscosity and ac-resistivity

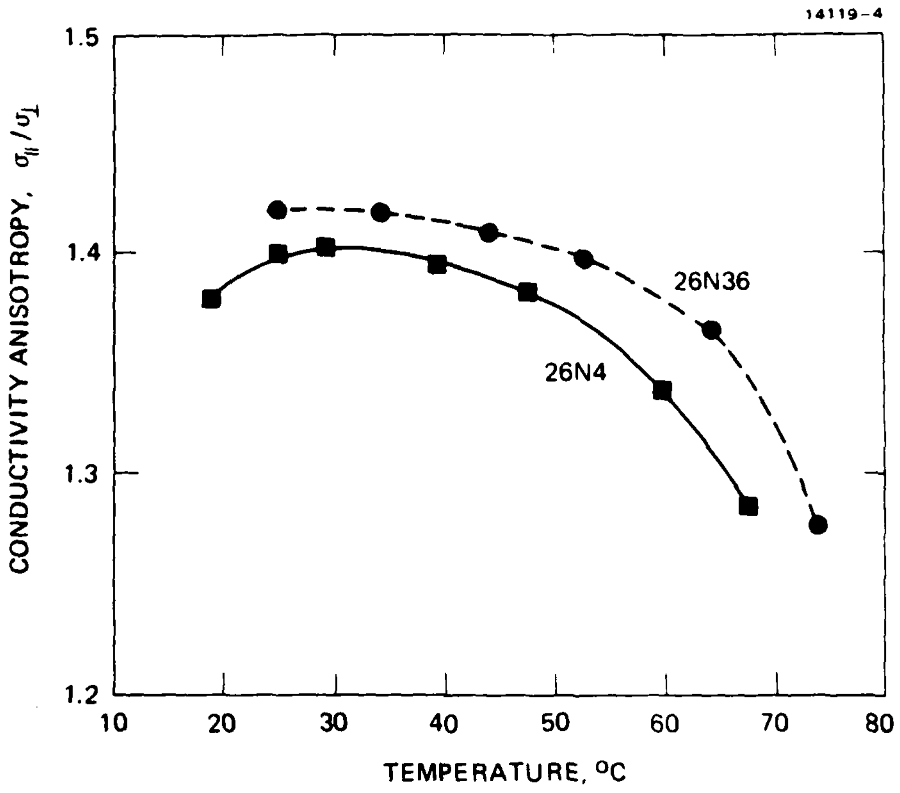


FIGURE 4 Effect of temperature on conductivity anisotropy.

HRL-26N36 are shown in Figure 6. In contrast to our observations that ac-DS is more efficient in thinner cells,[12] the scattering for dc-DS is not as high in cells of 6 μm as compared to 12 μm thickness. At higher temperatures (e.g., 60-65°C in Fig. 6) the scattering efficiency peaks at a lower voltage (10 to 12 V dc) and the %S falls off

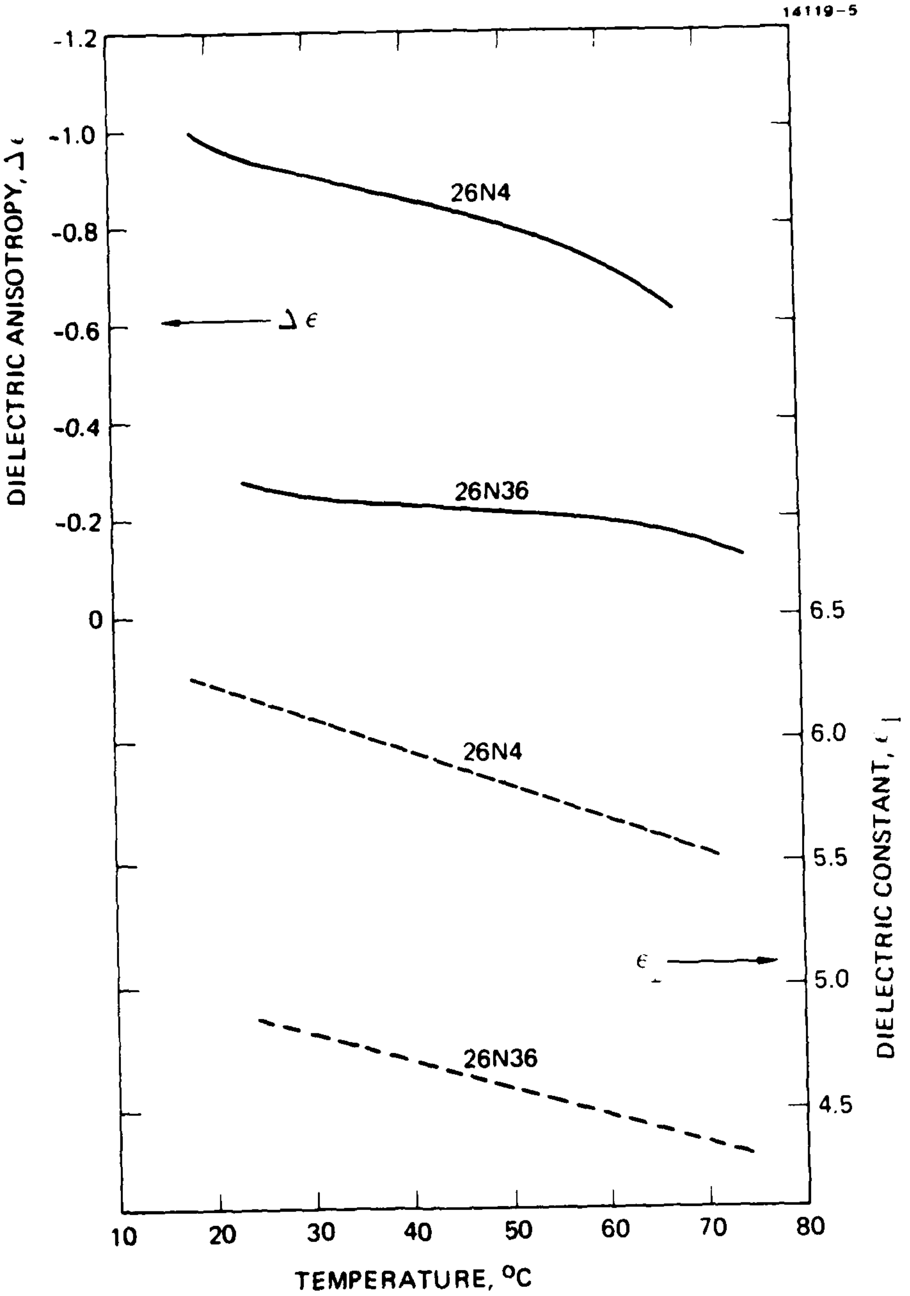


FIGURE 5 Effect of temperature on dielectric anisotropy and dielectric constant.

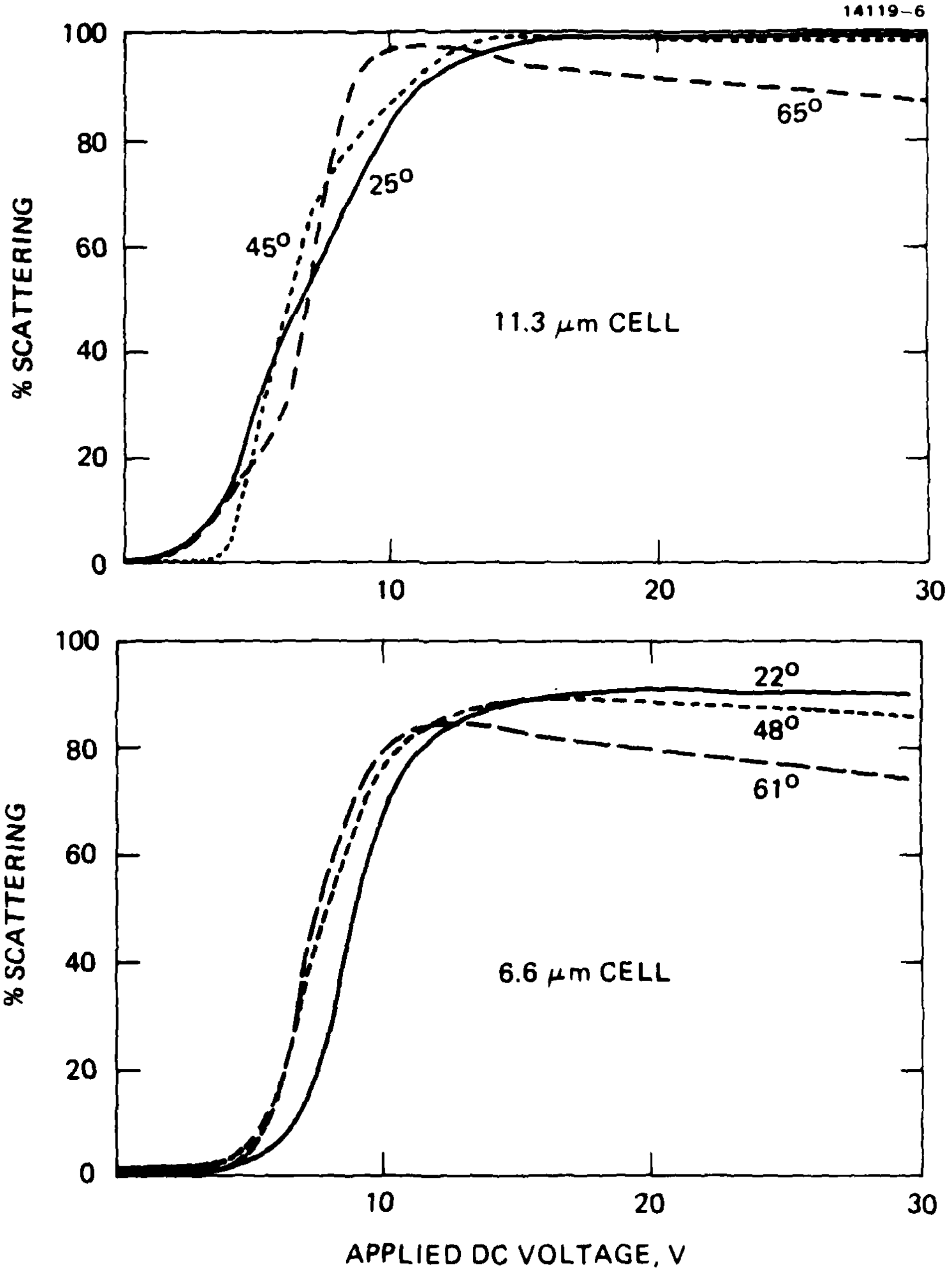


FIGURE 6 Effect of temperature and cell thickness on scattering curves for dc-DS.

at higher voltages. This higher voltage decrease in the dc-DS efficiency is more prominent at higher temperatures, in thinner cells, and in samples of lower resistivity. Because all of these factors cause higher current levels in the cells, we speculate that this higher voltage fall off of %S is related to a space charge build up at the PVA-coated electrodes.

The effects of elevated temperature and cell thickness on the DS response times of HRL-26N36 at 20 V dc are illustrated by the typical values shown in Figure 7, where the voltage is applied repetitively at 500 ms on and 500 ms off. In the highest temperature region the decay time increases with increased temperature, instead of decreasing as might be expected from the lower viscosity at higher temperatures. (We had observed the same effect previously[1] with other LC mixtures such as HRL-26N4.) Shorter length 20V pulses (e.g., 20 to 100 ms), or lower voltage pulses (e.g., 12 V), give higher %S and considerably faster decay times (e.g., 12 ms at 61°C in a 6 μm thick cell) for HRL-26N36 than the 500 ms voltage pulses of 20V. This is consistant with the idea that at high current levels a space charge build up may be formed that both limits the %S level and increases the decay time.

The response times shown in Figure 7 are equivalent to those previously observed for HRL-26N4, despite the fact that HRL-26N36 has a substantially lower viscosity. Nevertheless, the

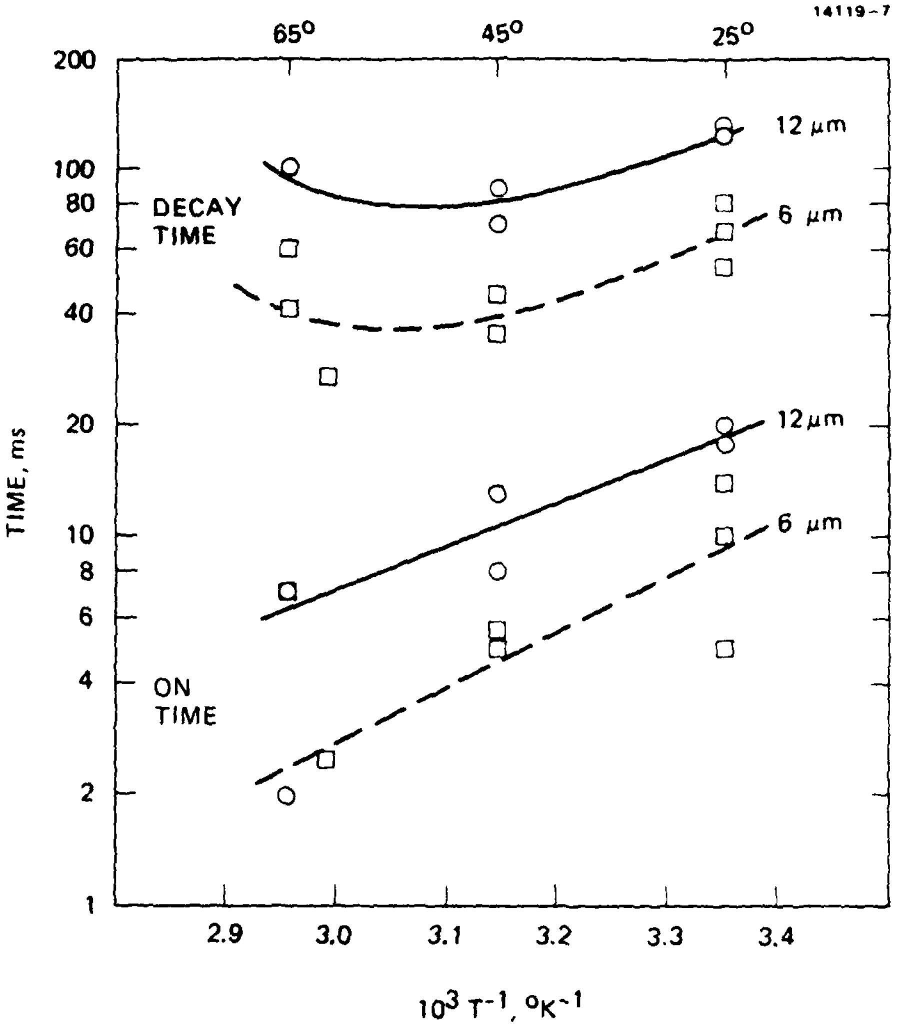


FIGURE 7 Effect of temperature and cell thickness on dc-DS response times at 20 Vdc.

fast turn on times at high temperature (e.g., 2 to 6 ms at 65°C in Fig. 7) are a small fraction of a typical 33 ms frame time for a pixel display.

This indicates that a high scattering level can be reached in a MOSFET matrix LCD even if the activating voltage on a pixel decreases during the frame time at high temperatures due to charge leakage from the pixel capacitor through the LC. For example, although the lowest resistivity sample used in Figure 7 had $\rho_{\perp} = 2 \times 10^8$ ohm-cm at 65°C, which is only one-fifth of the nominal resistivity of 10^9 ohm-cm required to maintain pixel charge at room temperature for 33 ms, the on time at 20 V and 65°C is less than one-fifth of this frame time period. In addition, because the %S is maximum in the 10 to 12 V range (see Figure 6), the effect of any capacitor charge leakage will be minimal until the voltage drops below 10 V. Thus, a full level scattering should be reached in a MOSFET matrix display at elevated temperatures and the average %S level during the frame time will depend primarily upon the decay time in the presence of residual charge on the pixel capacitor.

3.3 Sealant Thermal Stability Studies

A survey test was made on the compatibility of various sealant materials with an ester LC mixture at 100°C. A small sample of each sealant was individually cured in separate aluminum foil pans (DSC pans), then some undoped HRL-2N52 ester LC mixture[1] was added, a top was crimped onto each pan, and they were heated at 100°C for 120h in an oven. The LC was examined afterwards by placing it in a 13 μm thick cell with ITO electrodes and testing its resistivity and any impurity-induced DS at 20 V dc. The results are given in Table III, where a pick up of impurities by the LC from the previously cured sealant is shown by a lowering of the LC resistivity and by the presence of ionic impurities causing DS at 20 V dc. Because long life dc-DS operation requires the use of electrochemically reversible dopants, such as the HRL redox dopants, the presence of uncontrolled ionic impurities from the sealant is undesirable--and in fact their presence has been shown to cause very short dc-DS lifetime.[1] Of the fifteen different adhesives surveyed by the Table III tests, five (Nos. 2, 3, 4, 5 and 6) showed relatively little contamination and two others (Nos. 7 and 8) showed slight impurity contamination. We chose sealant Nos. 2 to 8 for further studies, and did not make further studies on the eight additional epoxies (Nos. 9 through 16) in Table III. The No. 8 sealant (Ablefilm 539 -Type II) was included mainly for reference purpose since we already knew that it introduces undesirable impurity dopants into the LC at elevated temperatures.[1]

Additional studies of the seven selected sealants were made in LC test cells with float glass/ITO/PVA substrates using 12.7 μm thick Mylar

TABLE III. Sealant Compatibility Test: Effect on Undoped HRL-2N52 LC After 120 Hours at 100°C.

	Sealant	Cure Temp. °C	Cure Time Hours	LC Resistivity ohm-cm	DS Due to Sealant Impurities
1.	None	----	----	7.87×10^{11}	None
2.	Polypropylene[a]	180	0.25	7.87×10^{11}	None
3.	Torr seal[b]			1.51×10^{11}	None
4.	TPA-84-HP[c]	145	1.5	1.46×10^{11}	None
5.	TPA-61	190	0.25	1.41×10^{11}	None
6.	Norland NOA-61[d]	(UV) 23	0.5	2.62×10^{11}	Slight
7.	Lens Bond M62[e]	70	1.0	5.62×10^{10}	Slight
8.	Ablefilm 539-Type II[f]	140	1.5	7.15×10^{10}	Little
9.	Able Bond 642-1[f]	100	1.0	5.25×10^{10}	Strong
10.	Able Bond 681-14[f]	175	1.0	5.25×10^{10}	Strong
11.	Lixon 1004 A/B[g]	100	2.0	4.04×10^{10}	Strong
12.	Transene Epoxy[h] 50-30-2	100	1.0	4.89×10^{9}	Strong
13.	Transene Epoxy 15[h]	100	1.0	1.71×10^{9}	Strong
14.	Transene Epoxy 13[h]	100	1.0	1.71×10^{9}	Strong
15.	Able Bond 342-13ACC[f]	70	2.0	4.25×10^{9}	Strong
16.	Devcon 5 Min Epoxy[i]	70	2.0	2.30×10^{9}	Strong

[a] Transparent Products

[b] Varian Associates

[c] ALX

[d] Norland Products

[e] Summers Laboratories

[f] Able Stik Labs

[g] Hitachi Ltd.

[h] Transene Co.

[i] Devcon Corp.

perimeter spacers. The cells were presealed except for a small filling hole for the LC. These cells were evacuated, back-filled with undoped HRL-2N52, and the filling hole was plugged with indium metal and overcoated with TPA-61 epoxy. The cells were heated at 100°C in an oven and examined periodically at room temperature for their resistivity and uniformity of alignment. The results are shown in Figure 8, where the apparent resistivity (assuming a nominal 12.7 μm thickness) is plotted and the first change in surface alignment is noted. During comparable heating times the cell with Norland NOA-61 sealant maintained a much higher resistivity (by one to two orders of magnitude) than the other sealants tested. It also showed a much longer heating time before any surface misalignment was observed. Even after 1830h of 100°C heating the misalignment in the Norland NOA-61 cell occurred around the filling hole, which had by then become unplugged. Because it was far superior to the other sealants in this test, Norland NOA-61 was chosen for dc-DS lifetime studies of the improved LC mixture in sealed cells.

The effect of moisture on the degradation of the Norland NOA-61 sealant was evaluated by testing one set of sealed cells immersed in water and another set in an atmosphere of 75% relative humidity. The results are shown in Figure 9, from which the activation energy of this sealant's degradation is found to be about 12 kcal/mole from

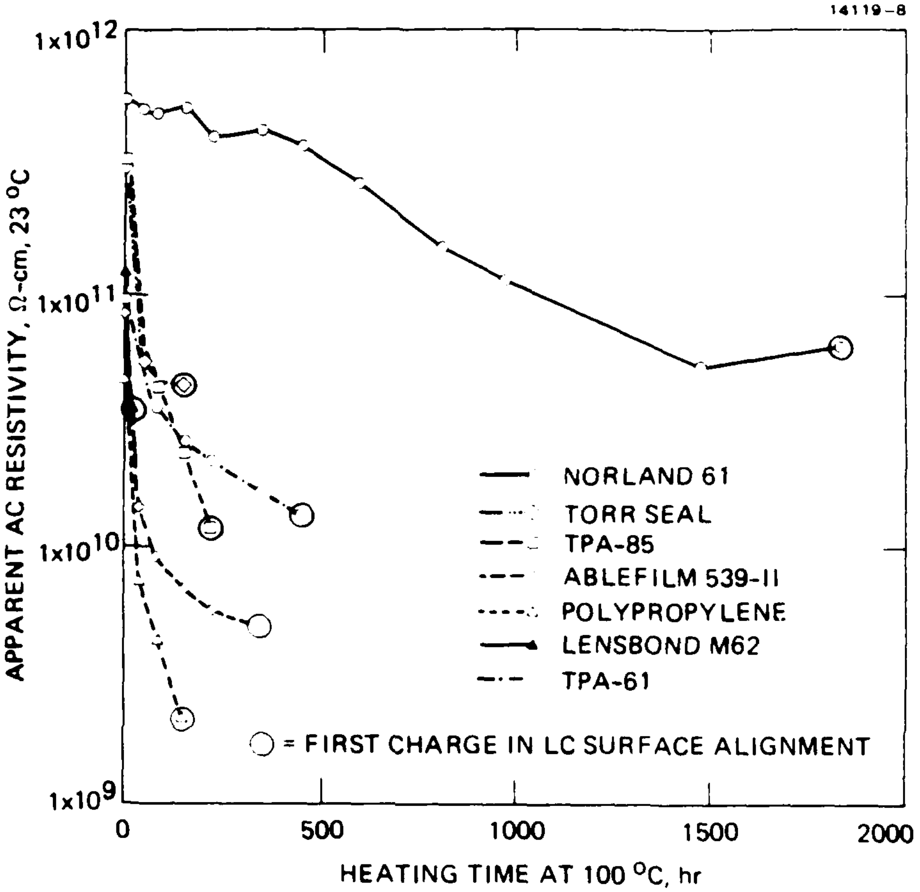


FIGURE 8 Sealant effects on resistivity and surface alignment of LC cells.

attack by both water and water vapor. These tests were made with a perimeter seal, using empty cells with a Mylar spacer. Evidence for sealant degradation was taken as the first noticeable change in the adherence of the outside edge of the sealant strip, from visual examination on a light table. The relative rates of degradation and the

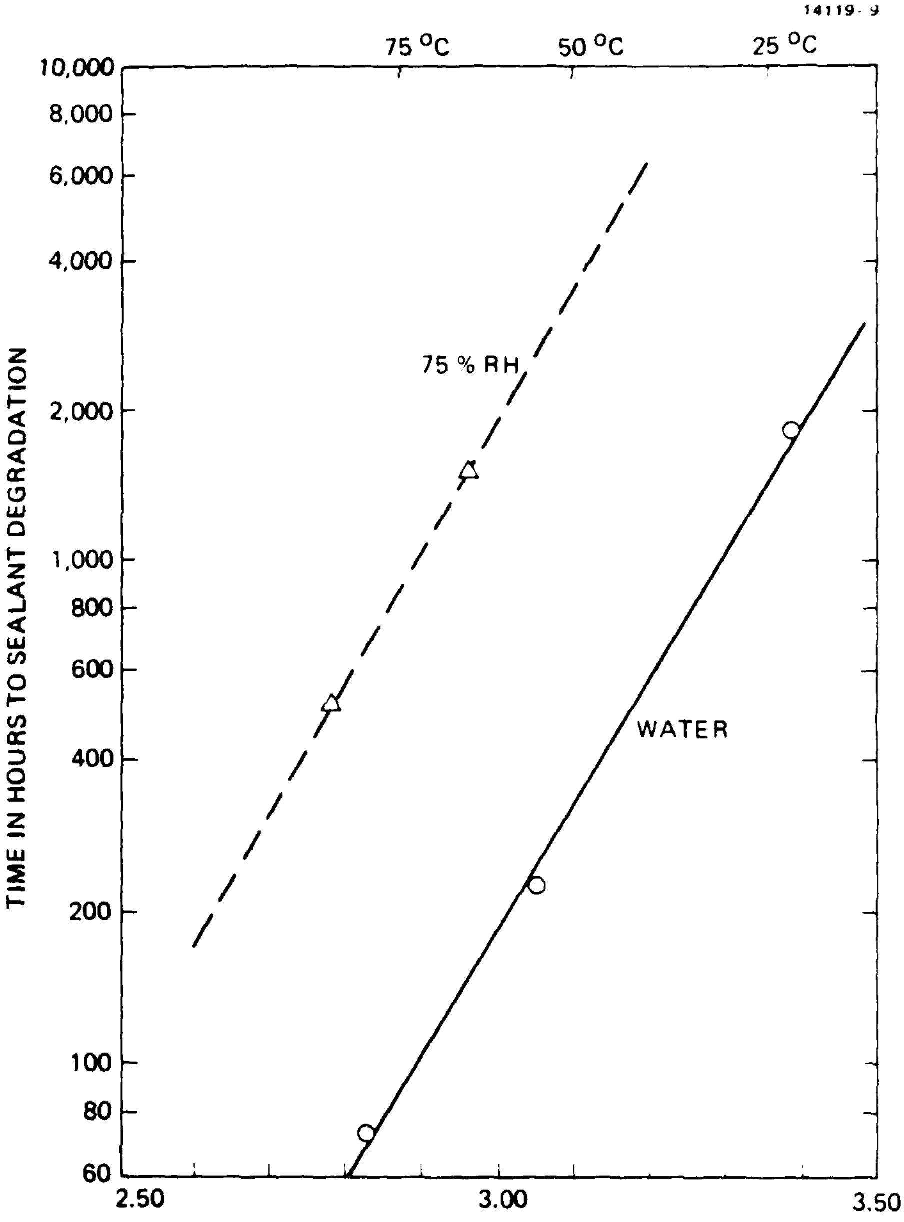


FIGURE 9 Rate of moisture degradation of sealan

activation energy are the important information gained from the Figure 9 data. Immersion in hot water was chosen as the first accelerated test condition, and the water vapor test results confirm that the activation energy for moisture attack is approximately 12 kcal/mole. This corresponds to sealant degradation times of about 16,500h and 1100h at 25° and 71°C, respectively, for Norland NOA-61 in a 75% relative humidity atmosphere. This is not a direct measure of the rate that water vapor will attack samples of LC in a sealed cell, which might be faster if water vapor migrates across (through) the sealant, and which might be slower if the entire width of the sealant has to be degraded first for the moisture to affect the LC. However, we expect that the 12 kcal/mole activation energy probably also pertains to the temperature dependence of the relative rates of moisture attack on the LC through this sealant.

3.4 Thermal Stability Studies on LC Materials and Cells

Accelerated tests were made on the thermal stability of the new LC mixtures with added redox dopants by heating the mixture in evacuated tubes at 100°C for long periods of time. The results are summarized in Table IV. Each doped LC became darker and more conductive after the 100°C heating, but the dc-DS characteristics remained essentially the same (as noted by $V_{90\%S}$) and no crystals or solid products were formed. We have found that the redox-doped ester mixtures generally become more conductive on standing, as indicated in Table IV for the resistivity of unsealed HRL-26N35 and -26N36 samples stored in a desicator at 25°C.

The thermal storage stability of redox-doped LCs at elevated temperature in sealed cells was studied by examining the effects of more than 3000h of storage at 80°C, as shown in Table V. The cells were pre-sealed with Norland NOA-61 optical cement around the perimeter spacer, were backfilled with LC after evacuation, and the filling hole was plugged with In and covered with the Norland NOA-61. The periods of heating, which totaled 3019h, caused no significant visual effects of degradation, i.e., no surface misalignment, no crystals, and no precipitates. This long period of 80°C storage of HRL-26N25 and -26N36 in the sealed cells caused little resistivity change. The dc-DS characteristics of two cells were not changed significantly by the heated storage, but in a third cell the higher voltage (16.1 V) required for 90%S indicates that some degradation occurred in this HRL-26N36 mixture--possibly the introduction of some ionic impurities with a lower conductivity anisotropy than the redox dopants.

TABLE IV. Thermal Stability of Redox-Doped LC in Evacuated Tubes at 100°C.

Conditions and Measurements[a]	HRL Mixtures and Results[b]			
	26N4	26N25	26N35	26N36
Resistivity (ohm-cm), $10^{-9}\rho$				
-Initial	2.5	2.7	7.1	8.9
-After 1173h at 23°C, in cell[c]	---	---	3.4	2.8
-After 100°C in evacuated tube	0.5	2.3	1.5	1.0
Heating time: 100°C, evac. tubes	2300h	837h	1173h	1173h
Visual color change from heating	darker	darker	darker	darker
dc Voltage required for 90% S				
-Initial	---	---	13.6V	11.9V
-After 100°C in evacuated tube	---	---	13.3V	11.7V

[a] Measurements made at 23°C in float glass/ITO/PVA cells with 25 μm spacers.

[b] Each LC doped with 0.5% each of dialkylferrocene (DBF or DHF) and TFM.

[c] Unsealed cell stored in desiccator.

TABLE V. Effects of 80°C Storage on Redox-Doped LCs in Sealed Cells.

Conditions and Measurements	HRL Mixtures and Results	
	26N25	26N36
Heated Storage time at 80°C	3019h	3019h
Resistivity (ohm-cm), $10^{-9}\rho$		
-Initial	5.0, 3.2	6.1, 7.6
-After heating	4.6, 4.6	4.7, 7.6
dc Voltage for 90% S		
-Initial	--, 14.8V	13.0, 14.6V
-After heating	--, 15.5V	16.1, 13.9V

[a] Measurements at 23°C in cells of float glass/ITO/PVA with 12.7 μm Mylar spacers, sealed with Norland NOA-61.

Low temperature storage effects on sealed cells of redox-doped HRL-26N25 and -26N36 were also examined, as indicated in Table VI. These cells showed no alignment changes or other ill effects from storage in the -60° to -20°C range, even though these temperatures are below their eutectic melting points. The changes in resistivity and in $V_{90\%S}$ are relatively small, indicating that the dopants remained in solution during the low temperature storage.

The electrochemical stability (i.e., dc-DS lifetime) of the redox-doped mixtures in sealed cells was studied at 55°C with 20 V dc applied continuously. The results of these experiments are summarized in Table VII and in Figure 10. The end of life of each cell was taken as the first observable defect, which was usually a brown deposit near the filling hole or along one edge of the perimeter seal. Most of the cells had lifetimes much longer than those we had found previously[1] using Ablefilm 539-Type II as the sealant for cells with other ester LCs at 55°C. The four best cells had lifetimes of 2312, 3091, 5279 and 6053h, which are all much longer than the lifetimes of unsealed cells studied previously.[1] This shows that these new LCs are capable of long operational lifetimes at elevated temperatures in well sealed cells. All of the cells in Table VII with short lifetime of <100h were sealed poorly and leaked. One-half of the cells with <100h lifetime had brown deposits next to the filling hole, where the LC might have had some contact

TABLE VI. Effects of Low Temperature Storage on Redox-Doped LCs In Sealed Cells

Mixture	Storage Temp. °C	Days of Storage[a]	Measurements After Storage[b] $10^{-9}\rho$(ohm-cm)	V for 90%S
HRL-26N25	23	(Initial)	3.4	---
	-60	12	3.7	---
	-40	7	3.7	---
	-20	7	3.5	---
HRL-26N36	23	(Initial)	7.4	13.0
	-60	7	6.6	13.0
	-40	33	4.8	12.9
	-20	31	4.2	12.5

[a] Sequential storage times

[b] Measurements at 23°C in cells of float glass/ITO/PVA with 12.7 μm Mylar spacers, sealed with Norland NOA-61.

TABLE VII. Sealant Quality Effects on Electrochemical Stability of Redox-Doped LCs at 55°C.

HRL Mixture[a]	No. Cells[b]	Distribution of Cell dc lifetimes[c] <100h	<1000h	<5000h	>5000h	Longest Life
26N25	12	5	4	2	1	5279h
26N35	2	1	--	--	1	6053h
26N36	4	--	4	--	--	789h

[a] Doped with redox pairs.
[b] Cells of float glass/ITO/PVA with 12.7 μm Mylar spacers, sealed with Norland NOA-61.
[c] Lifetimes with 20 Vdc at 55°C.

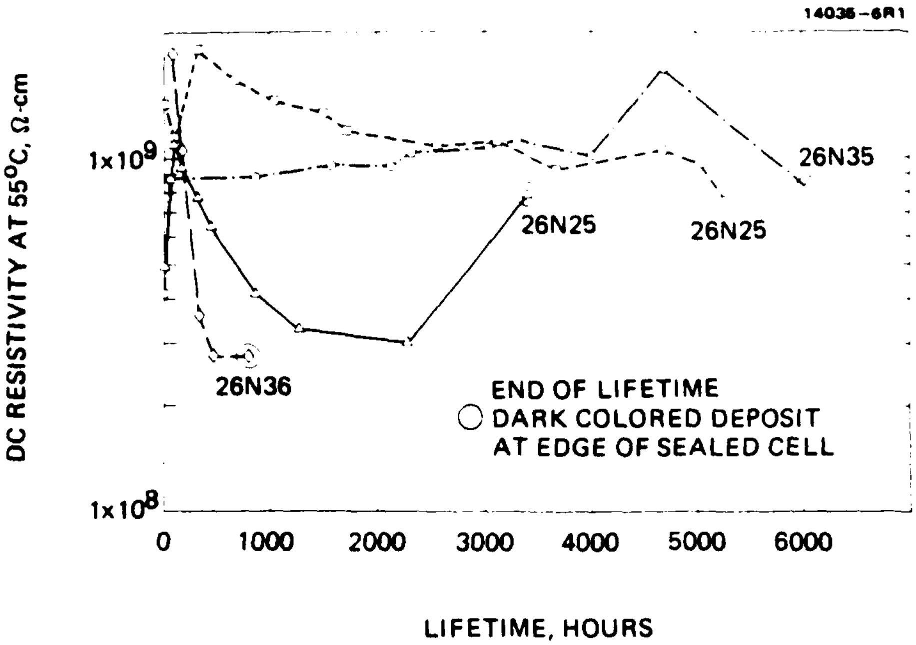


FIGURE 10 Sealant cell lifetime studies of dc-DS at 55°C.

with the uncured sealant that was placed over the indium plug and UV-cured. (On extended periods of dc-DS at 55°C the brown deposits became metallic looking deposits on the negative electrode, and were identified as iron by Auger analysis.) Other tests (55°C and 20 V dc) with redox-doped HRL-26N25 in unsealed cells (Mylar perimeter spacer only) showed a very short lifetime (<18h) in the presence of a small drop of the uncured sealant, a longer life (412h) in the presence of a drop of UV-cured sealant, and a long life (3400h) in the absence of any sealant. We believe that the shorter lifetimes in Table VII are due to impurities from incompletely cured sealant, whose electrochemical degradation effects appear to be accelerated by the leakage of air into the cells. Because there is a commonality of components in these three LC mixtures, the differences in the 55°C dc-DS lifetimes which are shown in Figure 10 are believed to be due to the quality of the seal rather than to differences in the purity of the different LC mixtures.

4. CONCLUSIONS

1. Of three new LC ester eutectic mixtures with lower viscosity which were formulated for DS applications, HRL-26N36 is superior to HRL-26N25 and -26N35 in the width of its nematic range (-15° to 78°C, undoped) and in its scattering level for dc-DS with redox dopants added.

2. Thinner cells show faster dc-DS response times than thicker cells, although with less change than the usual square of thickness relationship. However, thin cells show decreased scattering levels at high temperatures and high voltages (e.g.,> 50°C and >15 V). This may be due to space charge build up at the PVA-coated electrodes caused by the higher current levels.

3. At elevated temperatures the %S vs voltage peaks at intermediate voltages (e.g., 10 to 12 V),

and the ratio of decay-time/on-time increases. These effects and the fast on-times at the higher temperatures could compensate for a shorter length pulse, such as might occur in a MOSFET matrix display if the charge on the pixel capacitor leaks appreciably during a frame time due to the higher conductivity of the LC at high temperatures.

4. An optical cement, Norland NOA-61, was found to be superior to many other sealants (especially epoxy types) in its thermal stability with ester LCs at elevated temperatures. Well sealed cells showed that long term dc-DS stability is possible at elevated temperatures (e.g., >6000h at 55°C and 20 V dc). However, the lack of reproducibility in fabricating well sealed cells was found to be the limiting factor in the yield of long live dc-DS test cells.

5. The new mixtures with redox dopants show favorable long term storage stability in sealed cells between low and high temperatures of -60° to 80°C.

5. ACKNOWLEDGMENTS

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IMPROVED MATERIALS FOR DC DYNAMIC SCATTERING

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