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LIQUID CRYSTAL MATERIALS FOR MATRIX DISPLAYS.(U)
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LIQUID CRYSTAL MATERIALS FOR MATRIX DISPLAYS

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April 1982

Contract N00014–81–C–0307
Final Report
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By

J. David Margerum and Anna M. Lackner
Hughes Research Laboratories
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SECTION 1

INTRODUCTION AND SUMMARY

A. INTRODUCTION

We completed a full year of studies[1,2] in 1980 on "Liquid Crystal Materials for Matrix Displays" under ONR Contract No. N00014-79-C-0524, NR 359-713. The follow-on research program has been partially funded in the present contract. The overall goal of this program is to develop liquid crystal (LC) materials and techniques suitable for use in MOSFET* matrix displays being developed by Hughes Aircraft Company for several military applications, including an integrated head-up airplane cockpit display, a helmet-mounted display, a color alphanumeric display, a flat panel status advisory display, and a missile sighting system. The key LC material problems are related to requirements that such military displays must be storable over a wide temperature range (about -60 to 80°C) and must be operable in ambient temperature ranges between about -50° and 71°C. Because it is much easier to heat LC displays than to cool them, and also because *fast* response times (up to TV rate) are needed, our program is aimed especially at the use of LCs in the upper part of the operational range. Thus, our goal is to have displays that are operable up to 71° from ambient heating, and that are heated to a minimum cell temperature (probably in the 25 to 40°C range) when the ambient conditions are not warm enough.

The LC electro-optical technique that has been used in the Hughes matrix display is the dc-activated dynamic-scattering (DS) mode. The dc-DS has advantages over ac activation in permitting the use of simpler substrate circuitry, in operation at lower voltages, and in providing a good gray scale range. Redox dopants are used in ester LCs to give efficient scattering at relatively low voltages, and to permit long operational lifetime capability in the dc mode at room temperature. These dopants provide adequate conductivity and conductivity anisotropy for dynamic scattering, and they also protect the

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*MOSFET refers to the metal oxide semiconductor field effect transistors which are used as switches in the circuitry for each picture element in the silicon substrate of the LC matrix display.

LC by carrying essentially all of the current through the cell by means of the electrochemical reversibility of their oxidation and reduction reactions.

The research problems regarding the LC materials for the dc-DS matrix displays are centered on maintaining the integrity of the redox dopant and of functioning sealed cells over a wide range of temperatures. The sealant material must not contaminate the LC with impurities that significantly alter its conductivity, DS efficiency, electrochemical stability, and surface alignment. The thermal stability of the LC must be optimized for both storage and operational lifetime at elevated temperatures. The LC response times must be optimized for high contrast, TV rate pictures over a wide range of elevated temperatures when updated at 30 times/sec. The LC must have high dc-DS efficiency at lower operating temperatures (higher LC resistivity), as well as at higher temperatures (lower resistivity), and the ratio of decay-time/on-time must be optimized to widen the operational temperature range. (Otherwise, the LC has to be maintained between about 10^9 and 10^{10} ohm-cm, corresponding to a near $\Delta = 30°$ temperature range, for adequate dc-activation by the charge on each pixel of the matrix display.) Other key problem areas needing study are the stability of the LC surface alignment at low storage temperatures and at high operating temperatures, and the optimization of contrast and gray scale at wider viewing angles.

B. SUMMARY OF RESULTS

The research studies in the first ONR contract were directed toward evaluating the applicability of LC materials and cells for dc-DS at elevated temperatures, as related to the MOSFET matrix displays. Those results are summarized in the final report[1] and in a technical publication.[2] The research studies of the present contract were directed primarily toward key problems encountered at elevated temperatures due to interaction between the ester LCs and display cell materials.

In the task on Studies on LC Stability in Heated Cells, we investigated the causes for the formation of high-melting-point products from LCs heated in unsealed test cells. Methods were studied to avoid these undesirable thermal reactions by protecting the LC from oxygen, moisture, and surface effects, since the bulk LCs are quite stable in evacuated pyrex tubes heated at 100°C. We found that soft glass substrates cause thermal degradation. This is minimized in well-sealed, vacuum-filled cells in which the glass has protective layers such as conductive electrode with a thin polymer coating for alignment.

In the task on Studies of Sealant Effects in Heated Cells, the problem of excessive conductivity contamination of the LC by thermal interaction with the sealant materials was investigated. Improved sealants were found and were tested as a means to minimize the contaminants and thereby maximize the control of LC conductivity by redox dopants that are suitable for dc dynamic scattering. One ultraviolet-cured sealant showed no apparent LC contamination or degradation effects after more than 1800 hrs of 100°C heating with an undoped ester LC in a vacuum-filled test cell made with this sealant. The resistivity of this cell was 2 orders of magnitude higher than a similarly tested cell made with the standard sealant previously used in MOSFET matrix displays. This test also confirmed that our LC ester mixtures are basically stable at high temperature when used as a thin layer in glass cells with transparent electrodes.

In the task to Evaluate Temperature and the DC Activation Effects on Surface Alignment, the stability and uniformity of LC surface alignment in test cells were studied as a function of cold storage, hot storage, and dc activation at warm operational temperatures. We found that polyvinyl alcohol (PVA) coatings on conductive glass electrodes show good thermal stability in LCs studied in sealed cells, even at accelerated conditions of 100°C. However, the dc-operational stability was very short lived at only 55°C in test cells made with the standard epoxy sealant films previously used. Relatively long dc lifetimes are expected to be feasible in cells sealed with the UV-cured optical cement.

In the task on Studies on Improved LCs for Wide Temperature Range we examined improved LC materials. Revised compositions were utilized to obtain wider temperature range, better thermal stability, and lower viscosity. Because the viscosity strongly affects response, we proceeded with this task as part of our studies on response time optimization. We were able to use new LC materials (recently formulated on our internal HRL research project) for these studies. These new LCs have considerably lower flow viscosities than the mixtures that we studied previously. Test results on two mixtures show high conductivity anisotropy and excellent dc-DS curves. Thermal stability tests showed good long term bulk stability for redox-doped LCs with one of the new mixtures tested at 100°C in evacuated tubes.

C. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

The stability of ester LCs in display test cells is highly dependent upon the substrate surface and the cell sealant material. Thermal degradation via hydrolysis-type reactions is greatly accelerated by soft glass surfaces. Pyrex is recommended for use in place of float glass as the substrate window material in MOSFET matrix displays. Cells must be hermetically sealed for long term LC thermal stability. Previously used Ablefilm 539 sealants introduce impurities that cause rapid electrochemical degradation of LCs, even with redox dopants present. Norland 61 optical cement, which introduces about two orders of magnitude fewer conductive impurites (at 100°C) than the Ablefilm, is recommended for detailed study as an improved selant material for dc-DS cells operated at elevated temperatures. New low viscosity LC ester mixtures have better dc-DS characteristics than earlier mixtures, and have similar nematic temperature ranges. One of these (HRL-26N25) shows excellent long term thermal stability in the presence of redox dopants. Similar formulations with higher clearpoints are recommended for development as improved LCs for dc-DS at elevated temperatures.

An additional five-point research program is recommended to help complete the studies of LC materials for matrix displays. The main tasks proposed consist of studies on: (a) the stability of revised LC mixtures with higher clearpoints and relatively low viscosity, (b) the dc-DS stability of these mixtures with redox dopants in sealed cells at elevated temperatures, (c) the dc-DS response times as a function of temperature and cell thickness, (d) the effects of cell parameters on dc-DS angular distribution of scattered light, and (e) characterization of the physical and anisotropic properties of LC/-dopant mixtures.

SECTION 2

RESEARCH RESULTS

A. STUDIES ON LC STABILITY IN HEATED CELLS

Our earlier results[1,2] showed that bulk samples of several LC ester mixtures (both with and without dopant added) are quite stable at 100°C in evacuated tubes. However, the same LC mixtures sometimes yield solid reaction products within a few days of 100°C heating in thin electro-optical test cells. Such products are particularly prevalent in unsealed test cells, even though they are heated in a nitrogen-flushed oven. Although some sealed test cells (vacuum filled) with PVA-coated ITO electrodes* have shown long-term LC stability at 100°C, other sealed cells have shown product formation. Preliminary results indicated qualitatively that both glass surfaces and traces of air "catalyze" this thermal instability. The reaction products come out of the LC mixtures as tiny crystals when the cells are cooled to room temperature, and they ruin the optical quality of the cells. These products melt at higher temperatures than any of the starting components. Since the clearpoint of the remaining LC solution is increased, the products may also have LC properties. It is, of course, very important to learn how to keep the ester LCs as thermally stable in electro-optical cells as they are in evacuated tubes.

We have used simpler LC ester mixtures, with only 2 or 3 components instead of 7 to 10, to study the effects of glass substrates on LC thermal degadation processes at 100°C. This has the advantage of permitting easier sample preparation, as well as making it much simpler to observe reaction products from the surface catalyzed thermal reactions. The three new eutectic mixtures shown in Table 1 were calculated and formulated. Their nematic temperature ranges were measured and their reactivity with glass substrates

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*PVA refers to a thin (500 Å) coating of polyvinyl alcohol which is spin-coated from aqueous solution and then oven-baked; ITO refers to a sputtered coating (400 Å) of indium tin oxide used as a transparent conductor.

was checked. One of these (HRL-26N31) is a binary LC mixture and the other two (HRL-26N32, -26N33) are tertiary LC mixtures. All three formed crystals after 300 hours of heating in unsealed cells (N_2-flushed oven) made from ITO-coated float glass substrates. Mixture HRL-26N32 was chosen for further studies because its nematic melting point is far enough below 23°C to facilitate easy location of any reaction products that are crystalline at 23°C.

Table 1. Nematic Ester Eutectic Mixtures for Thermal Stability Studies

Mixture HRL No.	Components		Melting Point, °C		Clearpoint, °C	
	Code[a]	Wt%	Calculated	Observed	Calculated	Observed
26N31	10-[C]5	55.71	21.5	23	65.5	61.4
	60-3	44.29				
26N32	10-[C]5	38.11	11.6	18	71.0	69.7
	60-3	29.55				
	60-00C5	32.25				
26N33	20-[C]3	26.47	16.7	21	73.7	72.1
	60-3	34.75				
	60-00C5	38.78				

[a] See References 1 through 4 for structure code identification and for pysical properties of the components. Note that 10-[C]5 refers to 4-methoxyphenyl trans-4-pentylcylohexanecarboxylate, while 60-3 is 4-hexyloxyphenyl 4-propylbenzoate, etc.

Studies on the rate of thermal degradation of our HRL-26N32 tertiary test mixture with various substrate surfaces are summarized in Table 2. The most reactive glass surfaces (microscope slides, drawn glass, and float glass) showed decomposition rates (i.e., crystal formation) at 100°C in air-filled ovens similar to those in nitrogen-flushed ovens. Therefore, many of the accelerated tests were made in air-filled ovens as a means of controlling the amount of oxygen present. Tests were made to compare decomposition rates on float glass, pyrex, and quartz substrate surfaces and to study the effects of single and multiple coatings on them. Studies were also made on the uncoated substrates, as well as ones with ITO (indium tin oxide) coatings and wth Si_3N_4 (silicon nitride) coatings. (The Si_3N_4 is deposited by reactive sputtering using a Si target and NH_3 and Air gases.) Multiple coating of several variations were used, including ITO, PVA (polyvinyl alcohol), and sputter-deposited SiO_2.

In general, the rate of crystalline product formation was an order of magnitude slower in pyrex and quartz, and on all of the coated substrates as compared to the uncoated float glass, drawn glass, and microscope slide. However, the LC stability did not vary in any consistent manner with the choice of the coating layers, which were ITO, ITO/PVA, Si_3N_4, Si_3N_4/ITO, and Si_3N_4/ITO/PVA. This suggests to us that their lifetime was limited by the amount of moisture or oxygen diffusing into the cells across the Mylar spacer section, rather than by the particular coatings used in these tests.

Decomposition effects were observed fairly rapidly even in evacuated sealed cells when the surface was drawn or float glass. A sealed cell with float glass/ITO/PVA surfaces appeared to be much more stable, but unfortunately the cell leaked in the course of the experiment.

An attempt was made to distinguish between the relative importance of moisture and oxygen in the surface-catalyzed LC thermal degradation. Float glass test cells were filled with HRL-26N32 and heated in a dry oxygen or dry nitrogen atmosphere at 100°C, and were monitored periodically for decomposition product formation. The same experiments were repeated in oxygen and nitrogen bubbled through water. The thermal stability of the LC at 100°C in dry nitrogen, dry oxygen, water-saturated

Table 2. Substrate Effects on the Thermal Decomposition of Ester Mixture HRL-26N32 in Unsealed Cells[a]

Substrate Coating(s)[c]	Atmosphere	Hours of 100°C Heating to Produce Crystals in Thins Cells[b]				
		Microscope Slide	Drawn Glass	Float Glass	Pyrex	Quartz
None	Air	2-3	3-6	7-26	150-265	45-265
	N_2	-6	2-6	7-41	104-199	271-
	(S.C.)[d]		-24	-24		
ITO	Air			90-200	26-200	26-200
	N_2			104-312	199-312	
ITO/PVA	Air			26-265	26-265	26-265
	(S.C.)[d]			(953)[e]		
Si_3N_4	N_2	71-85	160-208		160-208	
Si_3N_4/ITO	Air			26-265	26-265	26-200
Si_3N_4/ITO/PVA	Air			67-265	45-265	67-200
SiO_2/ITO	N_2		199-312			
ITO/SiO_2	N_2			104-312		

[a] The cells have perimeter Mylar spacers of 12.7-μm thickness.

[b] The range of heating hours shown are from the first observation of cyrstals, to the formation of many crystals in the cell after cooling to room temperature.

[c] The nominal thicknesses of the coatings are: 400 to 600 Å ITO, 500 Å PVA, 4000 Å Si_3N_4, 2000 Å SiO_2.

[d] Sealed cell made with Norland 61 optical cement. (Evacuated, backfilled, plugged.)

[e] This cell leaked in the course of the experiment.

oxygen, respectively, showed little distinction when the cells were observed at room temperature for alignment change or crystalline decomposition products. We observed that LC alignment changes started after 4 hours of heating in all unsealed test cells, regardless of the type of atmosphere, and crystal formation started between 7 and 15 hours in all cases. After 86 hours of total heating time at 100°C, the test cell in nitrogen had the lowest crystal density. The atmosphere surrounding the heated cells had little effect on the initial cystalline product formation. However, moisture and oxygen may have been picked up or lost by diffusion around the Mylar spacer when the cell was examined in the room. Hydrolysis is believed to be a factor in the glass-catalyzed thermal decomposition of the LC.

An additional stability study was done using just the low melting 60-[C]4 (4-hexyloxyphenyl trans-4-butylcyclohexanecarboxylate) liquid crystal at elevated temperature. Thermal degradation of this single component appears to be slower than the tertiary mixture of HRL-26N32, which contains the 10-[C]5, 60-3, and 60-00C5 LC components. In an unsealed cell of float glass/ITO, the first crystals appeared in 60-[C]4 ester after heating a 13-μm layer for 880 hours at 100°C in an unsealed cell with float glass/ITO substrates. The LC developed microcrystalline products which melted in the 88° to 195°C range in the LC. Analysis by thin-film chromatography and by liquid chromatography each showed three or more new product peaks. However, neither infrared nor nmr spectroscopic analysis provided a clear indication of the structure of the products, which are a relatively small part of the small LC sample. A larger surface-area unsealed cell of 60-[C]4 in drawn glass was heated at 100°C for long time periods and various decomposition products were tentatively identified. The products were separated by thin layer chromatography and studied by IR microspectroscopy This analysis showed the presence of an aliphatic carboxylic acid (presumably cyclohexanecarboxylic acid) and of another product with a carbonyl group different from 60-[C]4. The presence of the acid indicates that some hydrolysis occurred, probably due largely to moisture picked up from the air. The drawn glass surface catalyzes the rate of this hydrolysis. Other reactions probably also occur with oxygen, especially with any phenol formed by hydrolysis.

In summary, our studies on the 100°C thermal degradation of ester LCs on surfaces showed the following:

- Soft glass (microscope slide, drawn glass, and float glass) greatly accelerates the thermal decomposition of ester LCs heated in unsealed cells. The soft glass surface also causes LC thermal decomposition and surface alignment changes in sealed cells.
- Use of pyrex and quartz surfaces slows down the rate of LC thermal degradation (in unsealed cells) by one to two orders of magnitude compared to soft glass.
- Use of coatings (such as ITO or Si_3N_4) on float glass also slows down the rate of this LC thermal degradation in unsealed cells, and slows it down even more in sealed cells.
- Unsealed float glass cells heated in various atmospheres (dry N_2, dry O_2, wet N_2, wet O_2) all showed rapid crystal formation regardless of the type of atmosphere. Thus, the effect of the float glass is larger than the effect of the atmosphere in which the cells are heated.
- All of the unsealed cells heated in air showed LC decomposition, even with multiple coatings designed to passivate the glass. Thus, cells probably must be well-sealed to avoid thermal degradation.
- The identification of acids as LC composition products indicates that hydrolysis-type reactions are an important part of the degradation process. The early changes in LC surface alignment indicate that decomposition products accumulate on or react with the surfaces.

On the basis of these observations, we propose that the following hydrolysis related reactions should be considered as degradation mechanisms in the heated LC cells, especially on the soft glass surfaces:

- <u>Surface catalyzed hydrolysis</u>. The moisture in the LC could cause hydrolysis, catalyzed by Si-ONa at the glass surface. In unsealed cells, the LC would continuously pick up moisture, especially when the cells are cooled to room temperatures:

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(1)

- Reactions of surface hydroxyl groups. The free hydroxyl groups on the surface could react with LC, or with phenols in the LC:

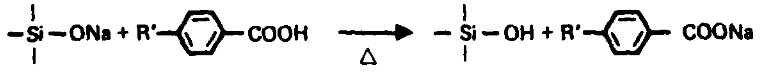
(2)

(3)

Reactions (1) and (3) could continue in a cyclic manner until all of the surface -OH groups are gone. This would strongly affect the LC surface alignment, as has been shown by the use of a process similar to reaction (3) in which long chain aliphatic alcohols are reacted with glass surfaces to control LC alignment.[5]

- Reactions of surface sodium ions. The alkali metal ions on the surface could undergo reactions that would put them into the LC:

(4)



(5)

Reactions (1), (3), and (5) could combine as a cyclic process, which converts the LC to carboxylic acid salts and surface-bonded phenolic groups until all of the surface alkali metal ions have reacted. The phenolate ions from reaction (4) would be particularly susceptible to air oxidation; the phenols from reactions (1) and (2) are also subject to oxidation. The introduction of the alkali metal ion products in reactions (2) and (5) would increase the LC conductivity. The carboxylic acid salts are, however, not very soluble and could cause crystal formation.

B. STUDIES OF SEALANT EFFECTS IN HEATED CELLS

Although we have successfully used adhesive-coated spacers as sealants for room temperature matrix display cells, these sealants cause several problems at elevated temperatures. These are (1) a lowering of the resistivity of the LC material, and (2) a change in the uniformity of the LC surface alignment. Our experience has been primarily with specially formulated epoxy adhesives (from Ablestik Laboratories) coated on Mylar films (Ablefilm 539, Types I, II, and III). These films are designed for controlled flow, low condensible volatiles, and use with LC displays. However, we have found that the conductivity contamination of purified ester LCs in heated cells (55 to 100°C) with these sealants is excessive in regard to the limited resistivity range desired for dc-activated dynamic scattering. In addition, the contaminants interfere with the electrochemical reversibility needed for dc-activation.[1,2] (Such reversibility is obtained, for example, when just the Hughes redox dopants[6,7] are present.) We have also observed surface misalignment effects after heating some sealed cells, particularly those with surface-‖ alignment obtained from ion-beam etched ITO, or from thin, evaporated layers of angle-deposited SiO on ITO. This may be due to contaminants that dissolve from the sealant into the hot LC and redeposit elsewhere on the surface during cooling. Although glass frit seals might cause fewer contamination effects than do organic sealants, the temperatures required for using glass frits are too high to be compatible with the matrix silicon substrate.

Alternative sealant materials were investigated to identify possible replacements for the Ablefilms. In our initial screening of a large number of sealants we used a simple test to measure their effect on LC conductivity and dynamic scattering. The best sealants from the screening test were used in evacuated test cells and their effect on the LC alignment was evaluated. The initial accelerated test method for conductivity change consisted of the following steps:

- A 3-6 mg sample of each sealant was placed in a small Al pan and cured according to manuacturer's specification.
- A 20-25 mg sample of HRL-2N52 (a phenyl benzoate mixture[1,2]) was added to each cured adhesive and the pans were crimp-sealed.
- The samples were placed in a 100°C oven for 120 hours.
- The LCs were removed from Al pans and their conductivities were measured in 0.5-mil-thick ITO test cells.

- Sealant contamination of LC was also observed by a 20 V dc signal across the ITO test cells. The undoped HRL-2N52 is a mixture of highly purified components with high resistivity ($\rho > 10^{11}$ Ω cm) that did not change when the LC was heated in the Al pan without sealants, and did not show any dc-DS. Therefore, the DS observed in some of the LC samples at 20 V dc was caused by the thermal decomposition products of the sealants.

In Table 3 we have summarized all of the different sealants that we evaluated, with their recommended curing cycle. The effect of heating is shown on their LC conductivity and dynamic scattering. Of the 15 different adhesives tested, four (Nos. 2, 3, 4, and 5) showed no DS and only small or no change in LC resistivity resulting from sealant contamination. The next three sealants (Norland 61, Lens Bond M62 and Ablefilm 539) decreased the LC resistivity to the $5 \times 10^{10} - 2 \times 10^{11}$ Ω cm range and they also caused some DS effects in the LC. We chose to evaluate sealant numbers 2 to 8 further for alignment effects, while studies on the eight additional epoxies (9 through 16) were discontinued due to the formation of highly conductive and strongly dynamic scattering contaminants in the LC.

Studies of the seven less reactive commercial materials were conducted in test cells made with float-glass/ITO/PVA substrates, with 1/2 mil Mylar spacers. The cells were sealed according to manufacturer's recommendation, and a small hole was left open for the introduction of LC. The cells were evacuated, back-filled with an undoped HRL-2N52 liquid crystal mixture, and the filling hole was plugged with indium metal and then covered by TPA-61 epoxy. All seven sealed cells initially showed uniform surface-parallel alignment when examined between crossed polarizers. Changes in surface alignment and in the resistivity of the LC was monitored periodically after heating the test cells at 100°C in air. After 348 hours of thermal treatment the cell sealed with UV-cured Norland 61 showed excellent alignment stability and very little change in the liquid crystal conductivity, as shown in Figure 1. Extended periods of cell testing are shown in Table 4, where the results are shown by the nominal resistivity of the LC sample, assuming a nominal

Table 3. Sealant Effect on HRL-2N52 LC after 120 Hours at 100°C

Sealants	Cure Temperature °C	Cure Time Hrs	LC Resistivity Ω cm	DS at 20 V dc
1. None	—	—	7.87×10^{11}	No
2. Polypropylene	180	0.25	7.87×10^{11}	No
3. Torr seal			1.51×10^{11}	No
4. TPA-85-HP[a]	145	1.5	1.46×10^{11}	No
5. TPA-61[a]	190	0.25	1.41×10^{11}	No
6. Norland 61[b]	23-uv	0.5	2.62×10^{11}	Very little
7. Lens Bond M62	70	1.0	5.62×10^{10}	Very little
8. Ablefilm 539-Type II	140	1.5	7.15×10^{10}	Little
9. Able Bond 642-1	100	1.0	5.25×10^{10}	Strong
10. Able Bolnd 681-14	175	1.0	5.25×10^{10}	Strong
11. Lixon 1004 A/B	100	2.0	4.04×10^{10}	Strong
12. Transene Epoxy 50-30-2	100	1.0	4.89×10^{9}	Strong
13. Transene Epoxy 15	100	1.0	1.93×10^{9}	Strong
14. Transene Epoxy 13	100	1.0	1.71×10^{9}	Strong
15. Able Bond 342-13ACC	70	2.0	4.25×10^{9}	Strong
16. Devcon 5 Min Epoxy	70	2.0	2.30×10^{8}	Strong

[a] American Liquid Xtal Company.

[b] Norland 61 is an optical adhesive cured at room temperature with uv light.

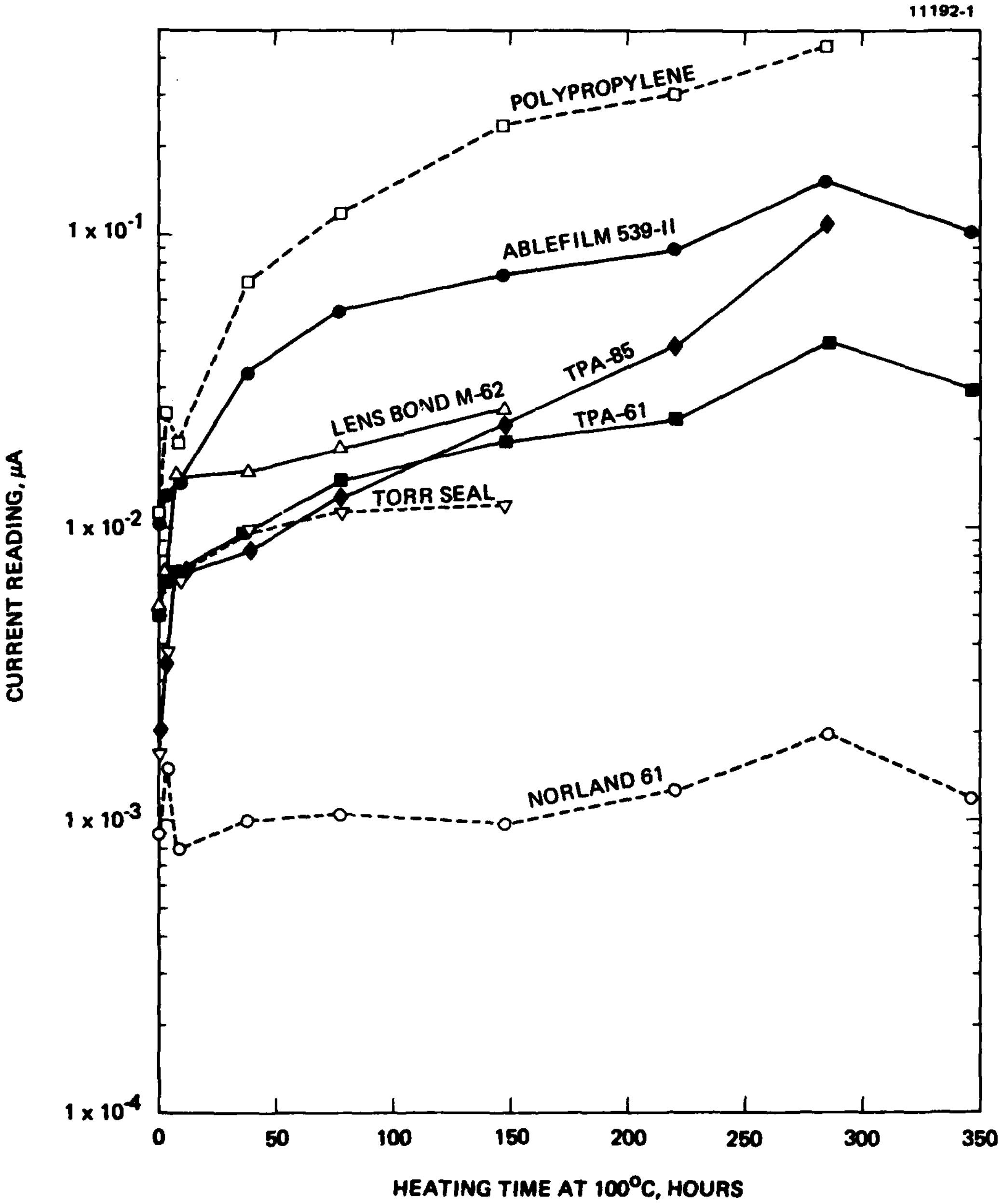


Figure 1. Relative room-temperature current of sealed cells after 100°C heating periods (measured with 0.1 V at 100 Hz in cells with nominal 0.5 mil spacing and nominal 1 sq in. area).

Table 4. Sealant Effects on LC Cells, After Heating

Sealant Type[b]	Nominal LC Resistivity after Heating[a]										Remarks
	0 Hrs	20 Hrs	140 Hrs	280 Hrs	450 Hrs	594 Hrs	971 Hrs	1475 Hrs	1836 Hrs	2989 Hrs	
None	4.2×10^{12}	(9×10^{10})	(2.5×10^{10})	(1.5×10^{10})	$9 \times 10^{9})$	(7×10^{9})	(5×10^{9})				In surface-∥, unsealed 0.5 mil cell.
Norland 61	5.6×10^{11}	5.9×10^{11}	5.1×10^{11}	2.7×10^{11}	3.6×10^{11}	2.6×10^{11}	1.1×10^{11}	4.8×10^{10}	5.8×10^{10}	3.3×10^{10}	Very good alignment at 1836 hrs except at sealing hole.[c]
TPA 61	9.4×10^{10}	6.4×10^{10}	2.7×10^{10}	1.2×10^{10}	1.3×10^{10}	1.1×10^{10}	8.4×10^{9}	4.8×10^{9}			Start alignment change at 450 hrs.
Ablefilm 539-II	4.7×10^{10}	2.5×10^{10}	6.9×10^{9}	3.4×10^{9}	4.1×10^{9}	4.0×10^{9}	4.0×10^{9}	2.7×10^{9}	3.9×10^{9}		Small alignment change after 348 hrs.
TPA-85	2.4×10^{11}	6.9×10^{10}	2.4×10^{10}	5.1×10^{9}							Alignment changed after 220 hrs.
Polypropylene	4.7×10^{10}	1.6×10^{10}	2.3×10^{9}	1.2×10^{9}							Alignment changed after 148 hrs.
Torr Seal	3.0×10^{11}	6.0×10^{10}	4.2×10^{9}								Few crystals at 38 hrs, broken cell
Lens Bond M-62	9.1×10^{10}	3.3×10^{10}	2.1×10^{10}								Alignment changed after 8 hrs.

[a] Nominal ac resistivity of HRL-2N52 at room temperature after heating at 100°C; cells had a nominal 0.5 mil thickness and a nominal area of 1 sq. in. Cells were float glass/ITO/PVA.

[b] Cells presealed with sealants before introduction of HRL-2N52. Filling hole plugged with In metal and sealed with TPA 61 epoxy.

[c] Alignment of the Norland 61 cell was also generally good after 2989 hrs of 100°C heating, but the plug seal had loosened and crystals were observed, especially around the fill hole.

thickness of 12.7 μm. The Norland 61 cell is about an order of magnitude better in retaining a high resistivity than the best of the other sealants. It is likely that the resistivity observed in the Norland 61 cell is actually caused by leakage of air around the filling hole, which became noticeably unplugged between 1836 and 2989 hours of heating. Since all of the other sealants showed serious decreases in LC resistivity or serious defects in surface alignment with less than 500 hours of 100°C heating, the Norland 61 optical cement clearly has superior properties.

In another test, we made float glass/ITO/PVA cells in which only two edges were pre-sealed with Norland 61; the other two were sealed after flowing the LC (HRL-2N52) into the cell. In other words, the final seal was made with the LC in contact with the optical cement prior to its polymerization by uv exposure. One cell with redox-doped LC was examined for alignment, conductivity, and dynamic scattering (at room temperature) after periods of heating at 100°C. Although this cell was not as stable as the pre-sealed cell in Table 4, it showed very little change after 440 hours of 100°C heating. This indicates that the Norland 61 should also be useful as a sealant to help plug the fill holes of sealed cells.

In our evaluation of sealants with LC at elevated temperatures we found Norland 61 to be the most stable. It is a one part adhesive which cures when exposed to ultraviolet light. The cure time is a matter of minutes and is dependent on the adhesive thickness and the uv light energy. Norland 61 is designed for bonding glass or metal substrates which have to withstand extreme environmental conditions. It is reported to have low viscosity, allowing a thin bondline, low shrinkage, and a resiliency that minimizes strain. Its chemical composition is proprietary; however, it is a clear, colorless liquid, and we were told that it is a urethane backboned hybrid photopolymer. The advantages of this adhesive for LC display sealing appear to be its thermal stability, its compatibility with liquid crystals, and its ease of operation. Since it is a one part system and 100% solid, it eliminates pre-mixing, drying, or heat-curing operations common to other adhesive systems. The Norland 61 is cured by uv light, with maximum absorption within the range of 354-378 nm. The cure is not inhibited by oxygen, and typically, the final adhesion can be accomplished in 10 min using a 100 W mercury lamp. The shelf life of the liquid sealant is at least 4 months if kept at room temperature.

In summary, the status of our studies on sealant effects in heated cells is as follows:

- Of the 15 sealants evaluated, the Norland 61 (uv curable optical adhesive), was the most stable at elevated temperatures of 100°C. No LC contamination or alignment change was observed after 900 hours of heating.
- The Norland 61 sealant has also been selected as one of the materials to be used in the final plug of test cells, since it does not react adversely with the undoped LC upon direct contact at 100°C.

C. ELEVATED TEMPERATURE AND DC ACTIVATION EFFECTS ON SURFACE ALIGNMENT

For high contrast and good gray scale in the matrix display, the liquid crystal has to be uniformly aligned parallel or perpendicular to the surface to give a non-scattering off-state. The preferred LC alignment in the matrix device is parallel to the electrode surface because this results in lower threshold voltage, several gray scale levels, and faster response times. Traditional surface-∥ alignment techniques such as rubbing are not applicable to matrix displays due to the lack of adequate uniformity and possible damage to the reflective substrate. The Hughes method[8] of angle ion beam etching (IBE) of the surface showed good alignment on reflective metal electrodes at room temperature, but on ITO the method is very sensitive to the presence of moisture[9] and is unstable at elevated temperatures. To achieve a uniform surface-∥ alignment that does not deteriorate at higher temperatures the electrodes need a protective coating that provides directionality to the LC and is also usable with dc activation. The two methods used presently are angle deposition of thin SiO_2 films and a thin coating of PVA polymer on the electrode, followed by IBE for directional alignment. Both methods are being evaluated with respect to alignment stability during storage at high temperatures, and to dc activation at operating temperatures.

Although fairly long periods of good dc-DS at 55°C can be obtained in unsealed cells,[1,2] the LCs are basically unstable in unsealed cells, as shown above. Cells sealed with Ablefilm 539 sealants (Type I and II) showed improved thermal stability with regard to surface alignment and crystal formation. (This is indicated by the 100°C results in Table 4, as compared to Table 2.) However, cells sealed with the Ablefilm epoxy coatings showed very short lifetimes of only 20 to 66 hours at 55°C with 20 V dc applied, whether the LCs were undoped or contained redox dopants. In short, the contaminants from the Ablefilm sealant completely limit the cell operational life at even modest evaluated temperatures.

The ester LCs show long term thermal stability in cells sealed with Norland 61; as shown in Table 4, the alignment, lack of crystals, and resistivity remained good after 1800 hours of heating at 100°C. Such sealed cells containing redox-doped LCs are expected to last for long periods of deactivation.

D. STUDIES ON IMPROVED LCs FOR WIDE TEMPERATURE RANGE

Results from our earlier research[1,2] showed that some of our LC compositions had favorable thermal, electrochemical, and dopant stability. The more stable mixtures contained the types of components shown in group A of Figure 2. The group B structures were less thermally stable, especially in the presence of the redox dopant. The group C structures in Figure 2 were of interest as additional components that have high clearpoints and might not unduly increase the viscosity of the mixtures. The viscosity data on the prior mixtures of good stability show that these mixtures have viscosities in the range of 48 to 64 cP at 25°C. In general, the lower viscosity mixtures such as HRL-26N3 and HRL-26N4 have faster response times, although response times also depend on many other factors, such as the elastic constant. Our time response measurements indicated that we needed new LC mixtures with viscosities lower than those of the three stable LCs previously studied. In addition, the LCs need to be optimized for low temperature storage; i.e., the solid that they form at low temperature should be either a glass or a eutectic mixture that will re-melt readily to give a homogeneous nematic state at as low a temperature as possible.

11826-2

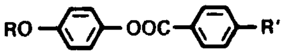
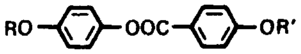
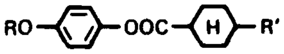
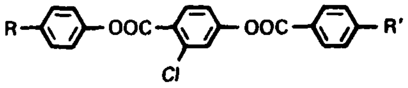
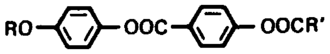
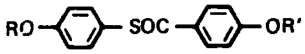
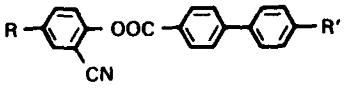
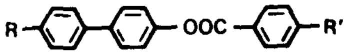
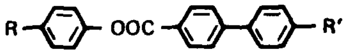
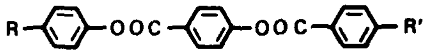
TYPE	CLASS STRUCTURE	CLASS CODE
A. GOOD THERMAL STABILITY		
PHENYL BENZOATE		RO–R'
PHENYL BENZOATE		RO–OR'
CYCLOHEXANECARBOXYLATE		RO–[C] R'
o - C1 DIBENZOATE		R–(Cl)OOCPR'
ACYLOXY		R–OOCR'
B. THERMAL INSTABILITY WITH REDOX DOPANT		
THIOESTER		RO-SR'
THIOESTER		RO-SOR'
o - CN BIPHENYL ESTER		R(CN)–PR'
C. OTHER COMPONENTS TESTED		
BIPHENYL BENZOATE		RP–R'
PHENYL BIPHENYLCARBOXYLATE		R–PR'
DIBENZOATE		R–OOCPR'

Figure 2. Types of components used in LC mixtures.

In a parallel HRL program we have studied revised calculated eutectic compositions in which the RO-OR' (p-alkoxyphenyl p-alkoxybenzoate) components in HRL-2N52, -26N3 and -26N4 are replaced by less viscous components such as the structures shown in group C of Figure 2. This is done to keep the clearpoints high while the viscosities of the mixtures are lowered. In related studies,[10] we have shown that RO-OR' compounds (such as 60-01 and 40-05)* substantially increase the viscosity of RO-R' mixtures, while RP-R' components of similar molecular length have less effect on viscosity and give a larger increase in clearpoint. We also used benzoyloxybenzoate diesters, R-OOCPR', without an o-chloro substituent as another means of lowering the viscosity while maintaining a high clearpoint. In order to utilize new components most effectively, we have assigned class viscosities,[10] and class dielectric constants to each class of ester structure considered for use in mixtures. We then revised our computer program on LCs so that when eutectic mixture compositions are calculated, the average molecular length, viscosity, and dielectric anisotropy are also calculated, as well as the melting point and clearpoint of the mixture. This is done by utilizing the values of length, η_{class} and $\Delta\epsilon$ class, for each component. Examples of the computer printout for two new eutectic mixtures are shown in Figures 3 and 4. The input data are the compound code and their melting point (MP), clearpoint (CLPT), molar heat of fusion (HF), molecular length (LEN), molecular weight (MWT), class viscosity (VISC), and class dielectric anisotropy (DEL). All of this information is stored in the system for each component. The calculated output data are the mole fraction (XI) and weight percent (Wt%) of each component in the eutectic mixture and the melting point, clearpoint, length, viscosity, and dielectric anisotropy of the mixture. This computer program greatly facilitates the process of seeking new mixtures which are likely to have desired values of nematic temperature range, viscosity, and dielectric anisotropy for DS applications.

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*Where 60-01 refers to 4-hexyloxyphenyl 4-methoxybenzoate, and 40-04 is 4-butoxyphenyl 4-pentyloxybenzoate.

```
#  COMPOUND        MP     CLPT     HF     LEN     XI      MWT     WT%     VISC     DEL

 1 20-3          75.70   68.00   6716.  19.67  0.0614  284.36   5.30   36.00   -0.25
 2 20-5          62.80   63.00   7492.  22.21  0.0674  312.41   6.39   36.00   -0.25
 3 60-5          40.90   59.30   5774.  27.03  0.2287  368.52  25.57   36.00   -0.25
 4 10-C5         40.90   71.30   5098.  21.40  0.2718  304.43  25.11   16.00   -1.30
 5 20-C3         49.00   79.80   6598.  20.21  0.1420  290.40  12.51   16.00   -1.30
 6 20-C5         56.90   85.90   7692.  22.59  0.0771  318.46   7.45   16.00   -1.30
 7 4-00CP4       88.50  186.00   5710.  28.31  0.0697  430.55   9.11  130.00    2.50
 8 10-00C3       81.10   84.50   7531.  20.06  0.0371  314.34   3.54   74.00   -1.00
 9 40-00C4       67.20   83.60   8191.  25.40  0.0447  370.45   5.03   74.00   -1.00

MIXTURE MELTING POINT= -2.288

MIXTURE CLEAR POINT= 79.162

MIXTURE LENGTH=  23.17

MIXTURE VISCOSITY=  35.84

MIXTURE DIELECTRIC ANISOTROPY=  -0.64
```

Figure 3. HRL-26N25, calculated eutectic mixture.

```
#  COMPOUND          MP     CLPT     HF     LEN     XI      MWT    WT%    VISC     DEL

 1 3P-4            93.40  182.30   4966.  25.55  0.0818  372.51   9.66  65.00    0.70
 2 20-3            75.70   68.00   6716.  19.67  0.0540  284.36   4.87  36.00   -0.25
 3 20-5            62.80   63.00   7492.  22.21  0.0584  312.41   5.79  36.00   -0.25
 4 40-1            72.90   53.00   7808.  19.61  0.0368  284.36   3.32  36.00   -0.25
 5 40-3            70.70   61.00   8150.  21.78  0.0344  312.41   3.41  36.00   -0.25
 6 60-3            51.80   57.40   5520.  24.44  0.1632  340.46  17.62  36.00   -0.25
 7 10-C5           40.90   71.30   5098.  21.40  0.2465  304.43  23.80  16.00   -1.30
 8 20-C3           49.00   79.80   6598.  20.21  0.1252  290.40  11.53  16.00   -1.30
 9 20-C5           56.90   85.90   7692.  22.59  0.0665  318.46   6.72  16.00   -1.30
10 10$5            63.80   70.30   5256.  21.43  0.1332  314.45  13.28  37.00   -0.04

MIXTURE MELTING POINT= -5.051

MIXTURE CLEAR POINT= 78.320

MIXTURE LENGTH=  22.07

MIXTURE VISCOSITY=  29.74

MIXTURE DIELECTRIC ANISOTROPY=  -0.60
```

Figure 4. HRL-2456N1, calculated eutectic mixture.

The HRL-26N25 mixture in Figure 3 and the HRL-2456N1 mixture in Figure 4 each show calculated values for a wide nematic temperature range and for a considerably lower viscosity than the ester mixtures we have previously studied.[1,2] The experimentally determined properties of these mixtures are summarized in Table 5. It should be noted that the experimental values are fairly close to the values calculated for these mixtures, including the viscosity and the dielectric anisotropy. These two mixtures were chosen for preliminary DS studies with the redox dopant pair of dibutylferrocene (DBF) and 2,4,7-trinitro-9-fluorenylidene-malanonitrile (TFM). The LCs doped with 0.5% DBF and 0.5% TFM were tested in $\parallel$-aligned and $\perp$-aligned unsealed test cells at 25°C. The scattering curves, shown in Figures 5 and 6, exhibit low threshold voltages and high scattering levels for both the HRL-26N25 and -2456N1 liquid crystal mixtures. The homeotropic (surface-$\perp$) alignment results in steeper scattering curves, and therefore reached the 90% scattering level at lower voltages (12 to 13 V) than the homogeneously (surface-$\parallel$) aligned cells (17 to 20 V). However, it can be seen that the homogeneous alignment provides a much better gray scale capability. The response times are also expected to be faster with the homogeneous than with homeotropic alignment.

Table 5. Physical Properties of Wide Temperature Eutectic LC Mixtures for Matrix Displays

HRL Mixture	26N25	2456N1
Nematic range,[a] melting point, °C	0[b]	0[b]
clearpoint, °C	73.9	73.8
Birefringence,[a] Δn	0.120	0.133
Viscosity[a] at 25°C, η in centipoise	31	27
Dielectric anisotropy[c] at 25°C ($\Delta\varepsilon$)	-0.59	-0.69
Conductivity anisotropy[c] at 25°C ($\sigma_\parallel/\sigma_\perp$)	1.436	1.547

[a] Measured without dopant added.

[b] Melting point observed after 1000 hours at -40°C in doped LC samples. Most of the mixture was liquid at -20°C, but the last few crystals did not melt until warmed to 0°C.

[c] Measured with 0.5% DBF + 0.5% TFM doped LC, $\rho_\perp = 2.5 \times 10^9$ Ωcm.

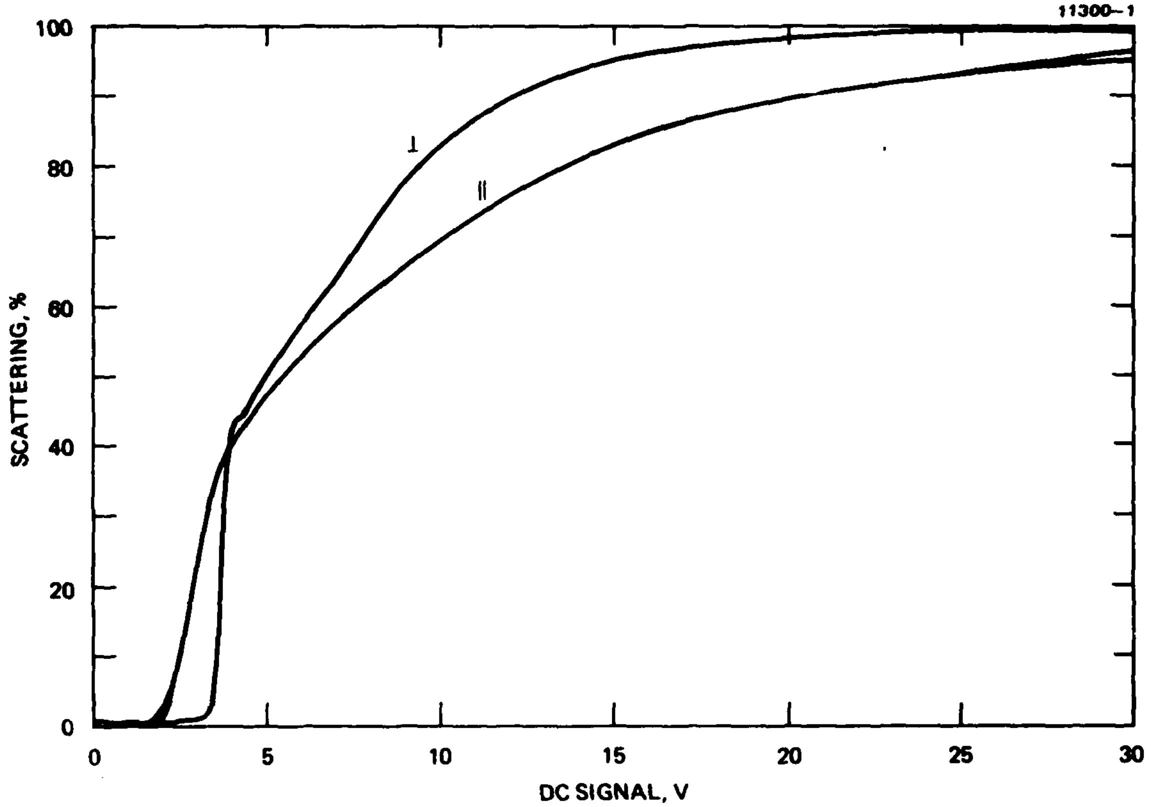

Figure 5. DC-DS curves for HRL-26N25 (0.5% DBF/TFM, 1/2 mil, 23°C.

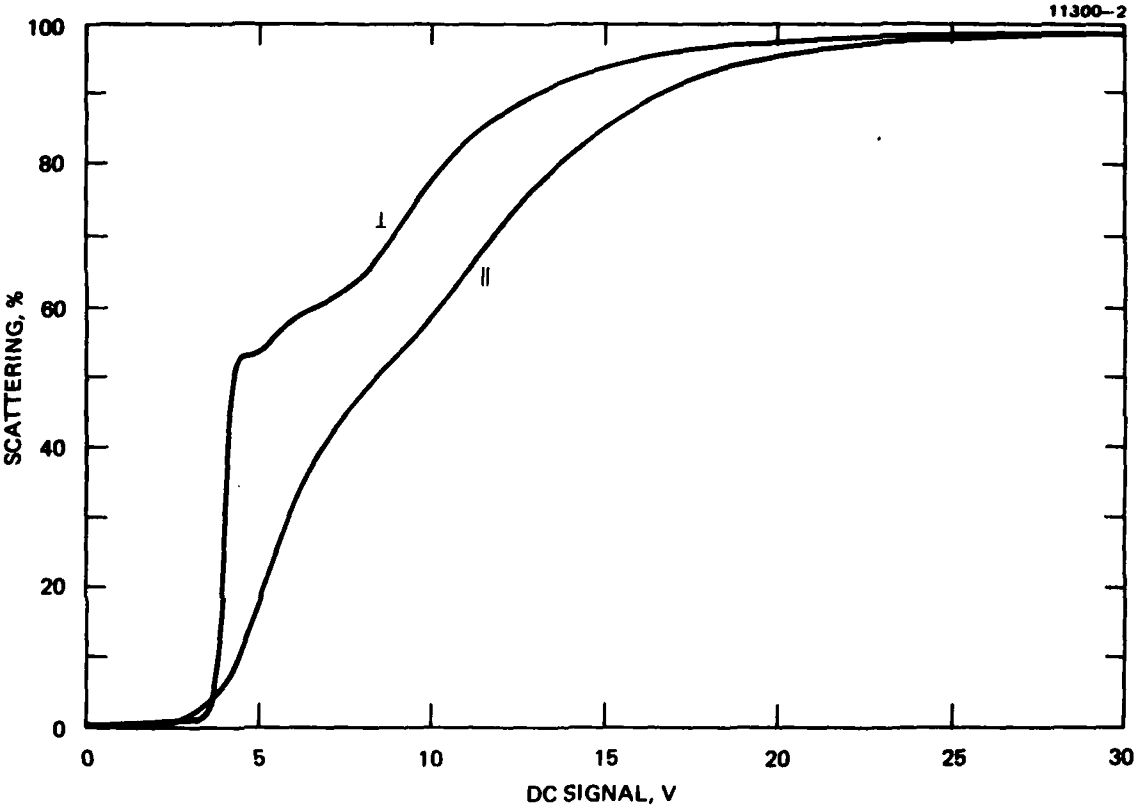

Figure 6. DC-DS curves for HRL-2456N1 (0.5% DBF/TFM, 1/2 mil 23°C.)

Tests were made on the bulk thermal stability of these new, low viscosity LC mixtures. The HRL-26N25 and HRL-2456N1 were made up with 0.5% redox dopants and were vacuum-sealed in glass tubes for bulk thermal stability tests at 100°C. Visual observation of the samples after 14 days at elevated temperature showed some darkening in color of the HRL-2456N1 mixture. After 28 days at 100°C, the HRL-26N25 LC mixture had a normal color appearance while the HRL-2456N1 LC mixture turned dark brown in color and some dark sedimentation was also observed. This latter mixture contains over 10% of the 10 -S 5 thioester component; these results are consistent with our earlier studies in which we found that thioesters were less stable than the corresponding phenyl benzoates. It is possible that the 3P-4 biphenyl benzoate component may also contribute to the thermal instability of HRL-2456N1 at 100°C. The HRL-26N25 mixture is clearly superior in regard to long term thermal stability, especially for continual operation at elevated temperatures. However, a revised LC mixture with a clearpoint somewhat higher than 73.8° is needed for better dc-DS characteristics at temperatures as high as the 71° operational goal.

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

We have found that the thermal and electrochemical stability of ester LC mixtures in cells are highly dependent upon the cell surface in contact with the LC and the cell sealant material. At accelerated test conditions of 100°C, ester LCs undergo hydrolysis-type reactions with moisture in the LC, and probably with surface hydroxyl groups and surface alkali metal ion sites as well. Soft glass surfaces greatly accelerate the LC thermal degradation, even in sealed cells. The LC thermal stability is better on pyrex and quartz surfaces, or on a soft glass (e.g., float glass) when it is coated with an indium tin oxide electrode and a polyvinyl alcohol alignment layer. We recommend the use of pyrex glass windows (with ITO/PVA coatings) on MOSFET matrix cells to minimize the effects of alkali metal ions at elevated temperatures.

We have also found that cells of ester LCs must be sealed from the atmosphere to obtain long-term thermal stability. The presently used Ablefilm 539 epoxy-coated films introduced conductive impurities into the LC at elevated temperatures; these impurities cause very short dc operational lifetimes of the LC, even when redox dopants are present. We have found that cells sealed with a uv-cured optical cement (Norland 61) introduce one to two orders of magnitude fewer conducting impurities into an undoped LC than does the Ablefilm. Because this optical cement also does not cause the surface misalignment problems observed with most other sealants, we recommend its study as a new sealant for dc-operation at elevated temperatures.

We have found that two new LC mixtures formulated for DS usage have a wide nematic temperature range, are considerably lower in viscosity, and have better DS characteristics than the LCs previously studied. One of these (HRL-26N25) shows excellent long term thermal stability with redox dopants, a nematic range of 0 to 74°C, a flow viscosity of 31 centipoise at 25°C, and low threshold dc-DS with good gray scale. We recommend further study of HRL-26N25, and the development of other related LC mixtures with somewhat higher clearpoints.

A continued research program has been proposed to conclude these studies on LC materials for matrix displays. The following tasks are considered to be the most important of these areas of study in order to reach the goal of developing LCs, substrates, and sealants suitable for dc activation of the dynamic-scattering mode so that the matrix display can be operated at elevated temperatures in the range of about 35 to 71°C and can be stored between -60 and 80°C:

- Prepare LC ester mixtures which have a nematic temperature range of about -5° to +80°C, a room temperature viscosity of less than 40 centipoise, and good dynamic scattering characteristics. Study their thermal stability with redox dopants at 100°C, and their low temperature freezing characteristics.
- Study the stability of ester LC mixtures in well-sealed cells, including the thermal storage stability at 80°C, the low temperature stability at -60°C, and the dc-DS stability at elevated temperatures e.g., 55°C). Examine the effect of these conditions on surface alignment, conductivity, and DS characteristics.
- Study the dc dynamic-scattering response times as a function of temperature (25 to 71°C) and cell thickness. Seek fast on-time and a high ratio of decay time to on-time in order to permit using doped LCs with resistivities $<10^9$ Ω-cm at elevated temperatures.
- Study the effects of cell thickness, surface alignment, voltage, and temperature on the distribution of scattering angles from dc-activated dynamic scattering in test cells.
- Characterize the physical and anisotropic properties of selected LC/dopant mixtures optimized for temperature range, stability, and dynamic-scattering characteristics. Study, particularly, the resistivity, flow viscosity, birefringence, dielectric anisotropy, and conductivity anisotropy as a function of temperature.

SECTION 4

RESEARCH PERSONNEL

The following research personnel participated in these studies.

Dr. J. David Margerum, Senior Scientist....Principal Investigator
Mrs. Anna M. Lackner, Member Technical Staff....Project Leader
Dr. Siu-May Wong, Consultant
Dr. John E. Jensen, Member Technical Staff
Mrs. Camille I. van Ast, Research Assistant Senior

SECTION 5

PRESENTATIONS AND PUBLICATIONS

1. J.D. Margerum and A.M. Lackner, "Ester Liquid Crystal Mixtures for Dynamic Scattering at Elevated Temperatures," Molecular Crystals Liquid Crystals, 76, 211-230 (1981).

SECTION 6

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Studies are made on liquid crystal (LC) and display cell materials related to the operation of MOSFET matrix displays in the dc-activated dynamic-scattering (DS) mode at elevated temperatures. Thermal degradation of ester LCs is accelerated by soft glass surfaces, which increase hydrolysis-type reactions. Pyrex, quartz, and coatings such as SiO_2, Si_3N_4, indium tin oxide (ITO), and polyvinyl alcohol (PVA) on soft glass (e.g., float glass) give less thermal degradation at 100°C

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than uncoated float glass or drawn glass. Hermetically sealed cells are necessary for long term thermal stability of ester LCs, although degradation occurs even in sealed cells when the LC is in direct contact with soft glass. Long term LC stability is observed at 100°C in sealed cells with ITO/PVA coatings on float glass. However, the epoxy type sealants previously used introduce harmful conductivity impurities into the LCs at elevated temperatures. These cause very limited dc lifetime, even at only 55°C and in the presence of redox dopants. An ultraviolet-cured optical cement is found to be a much better sealant; at 100°C it introduces two orders of magnitude fewer conductive inpurities into ester LCs and causes less surface alignment changes than epoxy sealants. Studies on new ester LC mixtures with relatively low viscosity show excellent dc-DS characteristics. One of these mixtures shows very good long term thermal stability in the presence of redox dopants at 100°C; it has a nematic range of 0° to 74°C and the following properties at 25°C: viscosity = 31 cP (or 31 centipoise), birefringence = 0.12, dielectric anisotropy = -0.59, and conductivity anisotropy = 1.44 with redox dopants. Recommendations are made for studies of these new LCs in pyrex cells sealed with optical cement and operated at elevated temperatures.

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