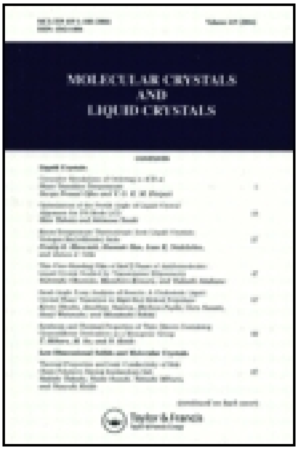

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Liquid Crystal Alignment Method for Long Lifetime Tilted-Perpendicular Light Valves

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Liquid Crystal Alignment Method for Long Lifetime Tilted-Perpendicular Light Valves

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A new technique for tilted-perpendicular alignment (TPA) of liquid crystals on surfaces greatly improved the photostability of the photoactivated liquid crystal light valves (LCLVs) with negative dielectric anisotropy liquid crystals. The operation of surface-perpendicular aligned LCLVs provided a very dark off-state, high contrast images, and high light throughput efficiency. Alkoxy groups bonded on angle-deposited SiO_2 gave controlled TPA, in which the tilt angle of LC on the treated surfaces was primarily dependent on the thickness of the shallow-angle deposited SiO_2 layer. We have demonstrated improved photostability to high intensity light exposures using this TPA method in hermetically sealed cells. Projection LCLVs with very high contrast and with greater than 10,000 hours of operational stability at 2000 lumens, were obtained using this new TPA method and more stable liquid crystal mixtures.

Keywords: liquid crystal, LC alignment, tilted-perpendicular, homeotropic, stability, light valve

1. INTRODUCTION

The operation of photo-activated liquid crystal light valves (LCLVs) using LCs of negative dielectric anisotropy with a small uniform-direction off-state pre-tilted surface-perpendicular alignment provides advantages such as a very dark off-state, high contrast images, and high light throughput efficiency.[1] In early LCLVs, the tilted-perpendicular alignment (TPA) was obtained by reacting a shallow-angle ion-beam-etched SiO_2 surface with an aliphatic alcohol, where the chain length was the main factor in determining the pre-tilt.[2,3] The LC degradation from high intensity ultraviolet (UV) and blue light decreased the pre-tilt and sharply limited the LCLV operational lifetime.[1] A new TPA method with well controlled tilt angles and long lifetime was reported for both older and newer types of LC mixtures.[4] Projection LCLVs with very long operating lifetime at high intensities are obtained by using the new TPA method and more stable, partially saturated, LC structures which have less blue light absorption. In this paper we describe the effect of exposure intensity, and exposure temperature on the TPA lifetime, and the improvement obtained by the exclusion of oxygen and moisture. In this paper we also compare the stability as a function of wavelength for our TPA LCLVs versus that of our lower contrast hybrid field effect (HFE) LCLVs.

2. EXPERIMENTAL SECTION

We have used a three-step process of the new TPA method[4] which consists of treating the conductive electrode with a 50–500 Å thick medium-angle deposition (MAD) of SiO_x followed by a 5–50 Å thick shallow-angle deposition of SiO_x coating laid down orthogonal to the MAD-SiO_x, and then reacting the surface with a long-chain aliphatic alcohol, by heating it in the presence of the alcohol in the liquid[3] or vapor[5] state at 140°C. Most of the studies were made using transparent test cells and LCLVs fabricated with the TPA alignment technique on 2.25″ diameter substrates with standard LCLV technology, using O-ring seals in the cell holders. The lamp exposure system[6,7] used for photostability studies, consisted of a 900 or a 1600 W ozone-free short arc xenon lamp with lens system, a 6 inch long water cell and UV cut-off filter system. Several techniques were used to observe photodegradation of the LC cells. In optical systems with a high intensity "hot" spot in the center area of the cell, visual observation (with field applied) of the change in LC surface alignment between crossed polarizers was used to denote the end of life. Change of electro-optical properties, LC resistivity, and LC tilt angles were also monitored at regular time periods. However it was more difficult to determine the end of lifetime with any of these methods than the visual method, because the analysis beam was larger than the hot spot.

Liquid crystal tilt angles were measured[3] at room temperature with the apparatus shown schematically in Figure 1. The perpendicularly aligned LC test cells were placed between crossed polarizers and were rotated from side to side with the nematic director lying in an orthogonal plane to the axis of rotation, forming a 45° angle with the incident polarized light.[8] When the light passed through the cell parallel to the optic axis, the transmission was at a minimum. The minimum transmission angle was determined most accurately by plotting the transmission as a function of rotation angle. The LC tilt angle was defined as the angle formed by the nematic director and the normal to the cell surface.

The effect of oxygen and moisture on lifetime was studied by exposing demountable and hermetically sealed small test cells with 1″ × 1″ aperture. The surface-alignment-treated electrodes were pre-sealed except for a small filling hole, using a highly stable[9] UV curable epoxy, Norland NOA61. These cells were evacuated, back-filled with the HRL-6N7 LC mixture,[10] and the filling hole was plugged and overcoated with epoxy.

The HFE mode transparent test cells and LCLVs were made by the Hughes Industrial Product Division using ZLI-1132 liquid crystal (E. Merck, Darmstadt) with 6.4 μm nominal spacing. The tilted parallel surface alignment was obtained by overcoating the conductive electrodes with 2000 Å straight sputtered SiO_2, followed by a 250 Å thick medium-angle deposited SiO_x, and a 25 Å thick shallow-angle deposited SiO_x coating laid down orthogonal to the MAD-SiO_x and assembled with a 45° twisted configuration between the two electrodes.

3. RESULTS AND DISCUSSION

Negative and positive dielectric anisotropy ($\Delta\varepsilon$) phenyl cyclohexanecarboxylates have been used for dynamic-scattering[9] and twisted nematic displays, due to their

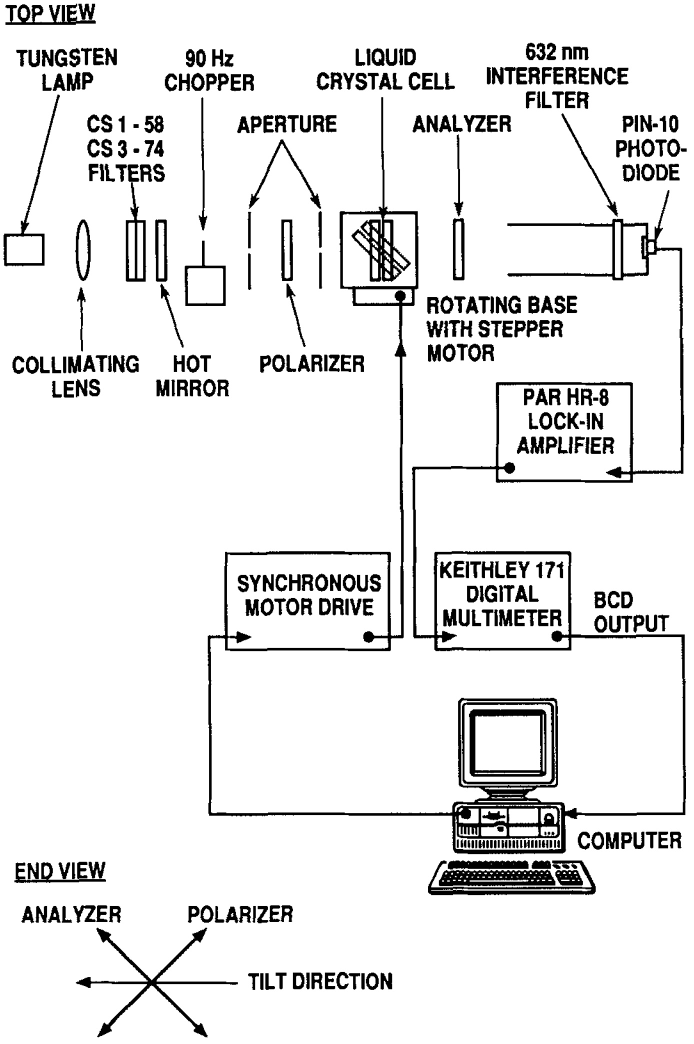


FIGURE 1 Apparatus for measuring tilt angles.

wide temperature range, low viscosity and favorable electro-optical properties. We were particularly interested in the negative $\Delta\varepsilon$ LC structures with an absorption edge in the UV and very small absorption tail in the blue region. The solution absorption spectrum of our three component phenyl cyclohexanecarboxylate mixture, HRL-6N7, was compared to the Merck ZLI-2857 mixture, and also to the Merck ZLI-1132 mixture, which contains 85% cyanophenylcyclohexanes and has been studied in our HFE-LCLVs. The spectra were taken in hexane solvent to avoid the light scattering problems in the neat LCs. In the 340 to 440 nm range, the HRL-6N7 had slightly lower extinction coefficient than the ZLI-1132 and ZLI-2857 mixtures as shown in Figure 2. All three of these mixtures are much less absorbing than the cyanobiphenyl LCs, such as BDH-E7 which was initially used

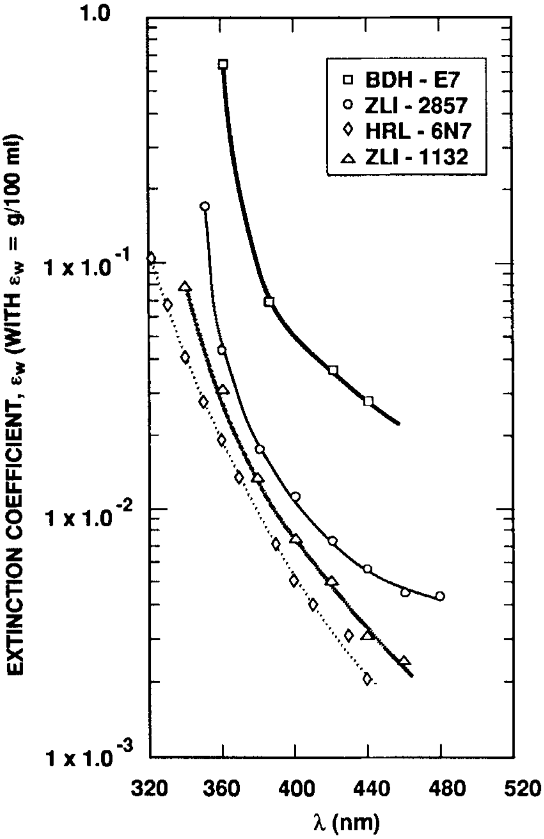


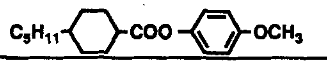
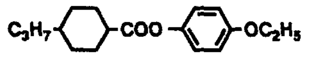
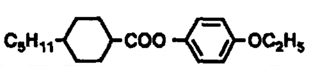
FIGURE 2 Solution spectra of liquid crystal mixtures in hexane.

in HFE-LCLVs.[6] Although the phenyl cyclohexanecarboxylate structures are less photochemically stable than the cyclohexylcyclohexane structures, studies made with the new TPA method using the HRL-6N7 mixture showed good LCLV stability to long exposures of high intensity. At room temperature this LC has a −1.34 dielectric anisotropy, a birefringence of 0.09, a low flow viscosity of 16 cP @ 25°C, with composition shown in Table I. Its nematic temperature range is 14.4 to 76.7°C.

Reproducibility of the TPA method was tested in three cells with 100/25 Å MAD/SAD SiO_2 surface coating treated with octadecanol in the vapor phase at 140°C. The off-state tilt angle varied from 1.3 to 1.9°, as measured with the apparatus shown in Figure 1. Electric field activated transmission data and the corresponding LC tilt angle are shown in Figure 3. The transmission measurements were made in a reflection mode between crossed polarizers positioned at a 45° angle with respect to the LC tilt direction. The off-state tilt angle of 1.7° off-perpendicular did not change until the voltage was above the 4.0 V threshold voltage. As the applied field increased the tilt angle, the transmission through the test cell also increased. At a transmission maximum, corresponding to the first tunable birefringent peak, we observed a 32° LC tilt from the perpendicular.

TABLE I

HRL-6N7 liquid crystal mixture composition

LC COMPONENTS	MOLE FRACTION
	0.497
	0.311
	0.192

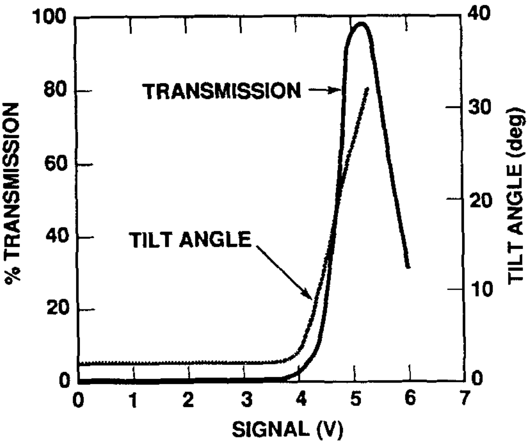


FIGURE 3 HRL-6N7 voltage activated transmission and LC tilt.

Photostability studies were initiated in an O-ring sealed LC test cell with half of the aperture exposed to the 900 W xenon lamp set up and filter system with less than 1% T at $\lambda \leq 360$ nm. After 420 Wh/cm^2 exposure surface misalignment defects were clearly noted on the exposed half of the test cell between crossed polarizers in the voltage activated state. The misalignment was worst around the cell edge, as seen in Figure 4, which may be an indication that oxygen diffused into the LC and accelerated the photodecomposition effects.

Figure 5 shows the pre-tilt changes observed with long term exposures of full aperture LCLV type test cells of HRL-6N7 using Xe lamp exposures with 1% UV cut-offs of 356, 376, and 406 nm, respectively. In these cells the ITO was first coated with 2000 Å of SiO_2 at normal incidence, followed by about 55 Å of MAD-SiO_2, 4–5 Å of SAD-SiO_2, and the C_{18} alcohol treatment at 140°C. The pre-tilt angles changed only slightly throughout the exposures, which were terminated at the first visual evidence of alignment nonuniformity in their field on-states (no

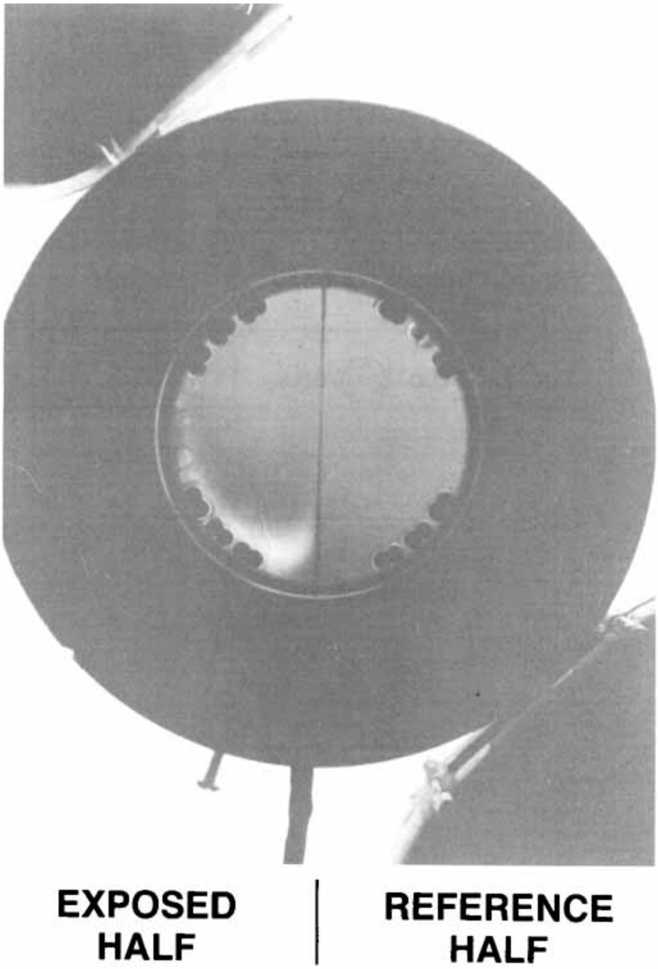


FIGURE 4 Liquid crystal alignment between crossed polarizers with 6.5 V activation signal. Left half of the HRL-6N7 test cell showing misalignment after 402 Wh/cm^2 exposure, $\lambda > 360$ nm. (Right half of the cell was blocked from this exposure.) See Color Plate II.

defects were observed in the off-state). The photostability was clearly a function of the UV cut-off filter wavelength. During the exposures, these cells all had voltages applied to induce a field tilt corresponding to a transmission maximum in an operational system. In Figure 6, the middle curve shows the TPA photostability lifetimes for six such HRL-6N7 cells (five test cells and one LCLV) as a function of the UV cut-off filter. With the 406 nm cut-off filter, we consider the upper point (which was an actual CdS-LCLV) much more representative than the lower point (which may have had some LC impurity) because the UV cut-off wavelength generally has a strong effect on the LC photostability. This LCLV exposure lifetime of about 2000 Wh/cm^2 corresponds to an operating lifetime of about 5000 hours with 2000 lumens of white light incident on the readout side of the LCLV.

The accelerated photostability studies with HFE mode test cells showed similar

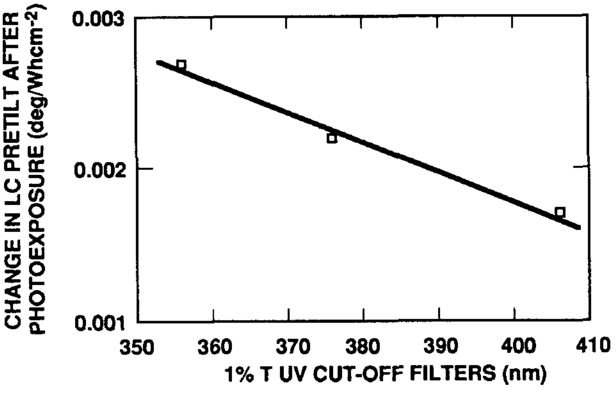


FIGURE 5 Pre-tilt photostability of HRL-6N7 in test cells with ITO coated sequentially with 2000 Å SiO_2, MAD/SAD SiO_2 (55/4 Å) and treated with octadecanol. A broadband Xe lamp exposure was used, with the UV cut-off filters indicated.

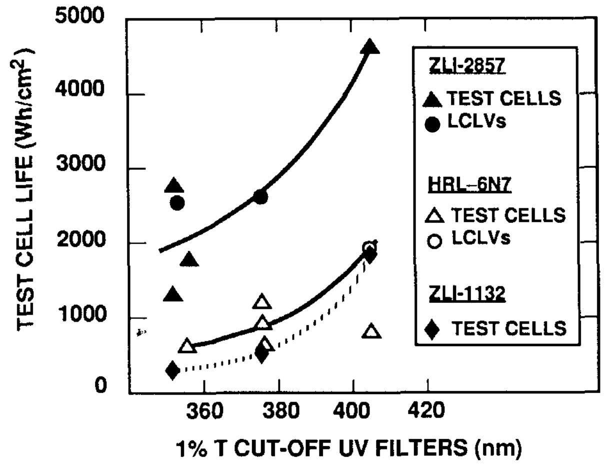


FIGURE 6 Photostability lifetime of LCs as a function of the filter cut-off wavelength for 1% UV transmission. Exposures were of test cells and LCLVs treated with the new TPA method for HRL-6N7 and ZLI-2857 mixtures, and are compared to HFE test cells with ZLI-1132 treated for surface parallel alignment.

wavelength dependence and lifetime as the HRL-6N7 cells, as shown in the lower curve of Figure 6. The ZLI-1132 LC photostability was increased from 380 to 595 and 1913 Wh/cm^2 when the cut-off filter (1% T) was extended further into the visible, 353 nm to 376 nm to 406 nm, respectively. The lifetime data as a function of cut-off wavelength (λ) are very similar for the HFE mode ZLI-1132 and TPA HRL-6N7; however, the contrast ratio of the tilted perpendicularly aligned LCLVs are several times higher as compared to the HFE LCLVs.

The effect of light intensity and elevated temperature were studied in an accelerated test using the 1600 W xenon lamp exposure system and 376 nm cut-off filter set up (1% T), with 1.7 W/cm^2 intensity at 57°C. Lifetime of the HRL-6N7 LC in a test cell under the above conditions was decreased to 751 Wh/cm^2 compared to the 801 Wh/cm^2 observed at a lower light intensity (0.5 W/cm^2) and temperature (37°C), indicating only a small change in photostability due to high intensity and increased operational temperature.

One of the major factors affecting the lifetime may be the presence of oxygen and a trace of moisture in the assembled LCLV units. Degradation of LC surface alignment, contrast, and cosmetic quality around the cell perimeter may all be indications of such effects. To determine the atmospheric effect on photostability, we compared the LC stability in hermetically sealed 1″ test units versus demountable 1″ test cells. The sealant material, Norland NOA61 optical cement, was selected because it did not contaminate or react with the HRL-6N7 LC, was thermally stable and rigid, and did not undergo photodegradation Accelerated photostability tests with the 1600 W xenon lamp and 356 nm cut-off filter set up were used to compare the LC lifetime in the sealed and demountable test cells. At the same time we compared the photostability of the new TPA alignment method to the prior technique[2,3] (alcohol treatment of the ion beam etched silica surface). Test data are summarized for these alignment methods in Table II. Very little increase in the average liquid crystal surface tilt from measurements prior to light exposure to tilt recorded at the end of lifetime. However, the LC lifetime in the hermetically sealed test units were 3–4 times longer than in the corresponding demountable units, indicating improvement in the LC photostability by the reduced oxygen and water concentrations. Also, the new alignment method resulted in 1.6 to 2.2 times longer lifetime than the old alignment method, although some of this improvement may be attributed to using exposure conditions without applied voltage for the new TPA method.

TABLE II

Photostability of HRL-6N7 in 1″ test cells exposed to 1600 W xenon lamp with 353 nm cut-off filter system

TEST CELLS	DEMOUNTABLE	SEALED	DEMOUNTABLE	SEALED
ALIGNMENT :				
- METHOD	NEW TPA	NEW TPA	OLD	OLD
- SiO_2 straight sput.	1500 Å	2000 Å	2000 Å	2500 Å
MAD/SAD	417 / 12Å	417 / 12Å	---	---
20° IBE	---	---	Yes	Yes
- ALCOHOL	$C_{18}H_{37}OH$	$C_{18}H_{37}OH$	$C_{18}H_{37}OH$	$C_{18}H_{37}OH$
SIGNAL	0 V	0 V	6.7 V	6.7 V
TILT OFF - ⊥ :				
- BEFORE	~ 12 °	4.4 °	1.6 °	0.9 °
- END LIFE	~ 14 °	4.8 °	1.9 °	1.9 °
LIFETIME : WH/cm^2	435	1289	198	815

Studies were also made using the LC mixture ZLI-2857 from E. Merck, which has a wider nematic temperature range, and a more negative dielectric anisotropy than the HRL-6N7. The ZLI-2857 near-UV absorption is slightly higher than the 3-component phenylcyclohexane mixtures, as shown in Figure 2. Test cells were made with it in glass-ITO substrates overcoated with SiO_2 or Si_3N_4, then coated with MAD/SAD-SiO_2 layers, and reacted with C_{18} alcohol. The pre-tilt angle variation with temperature was very low for these cells, between 0.006 and 0.012° per °C over the range of 20–64°C. We found that the pre-tilt angle varied linearly with the thickness of SAD-SiO_2 deposited on a fixed thickness of MAD-SiO_2. High contrast ratios were obtained with a small tilt in the 1–4° range, which was sufficient to prevent the occurrence of image-induced alignment mode defects in the LCLV projection pictures. Much longer LCLV tilt-photostable lifetimes were obtained with ZLI-2857 than with HRL-6N7 or with HFE mode ZLI-1132, in spite of the higher visible absorption tail of the ZLI-2857. These results (obtained with applied voltages on during exposures) are shown in the upper curve of Figure 6 for four test cells and two CdS-LCLVs. With a UV cut-off above 395 nm, the exposure lifetime was greater than 4000 Wh/cm^2, corresponding to greater than 10,000 hours of operational lifetime with 2000 lumens of white light on the output side of the LCLV. Analysis of the LC removed from the cells after these tests showed that substantial compositional changes had taken place in the LC during the exposures. The clearpoint of the LC had increased, and gas chromatographic analysis showed the presence of about 3% impurities, as well as changes in the ratios of the initial components. These results confirmed that this new TPA technique is unusually insensitive to the formation of photodecomposition products and to changes in the LC composition. In contrast, photodecomposition products of only about 0.1% in BDH-E7 caused surface alignment defects in HFE-LCLV cells.[6] The BDH-E7 lifetime was severely limited in exposure to high intensity visible light of a projection system, due to the small LC impurity absorption tail that extended into the visible, and leading to small amounts of polar photodegradation products. ZLI-1132 showed very slight absorption tail in the visible, however this polar impurity level increased after photostability tests. (For example, polar impurity levels of 1.6% decreased the lifetime of a ZLI-1132 sample to as little as 35 Wh/cm^2. At the same time a sample with only 0.03% impurity showed 412 Wh/cm^2 lifetime for 900 W xenon lamp exposure with 356 nm cut-off filter.)[7] The decomposition and subsequent realignment of ZLI-1132 in HFE LCLVs, which lead to failure were manifested by a decrease of contrast and resolution. The failure rate of ZLI-1132 was also accelerated by high light intensity and exposure to projection lights with cut-off filters below 420 nm.

4. CONCLUSION

A new technique for tilted-perpendicular alignment of liquid crystals on surfaces greatly improved the photostability of liquid crystal light valves. Alkoxy groups bonded on angle-deposited SiO_2 gave controlled TPA angles, resulting in high contrast LCLVs with greater than 10,000 hours of operational stability at 2000 lumens. The high contrast ratios (>180:1) permit the combined use of three LCLVs (red, blue, and green) in full color projection displays with a black off-state and greater than 60:1 contrast ratio. The photostability is greatly dependent on liquid crystal structure and its absorption tail in the near-visible range of the spectrum. The lifetime can be further extended by the exclusion of oxygen/moisture with the use of hermetically sealed cells.

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