生成機制の研究及びその評価手法
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Generation mechanism of residual direct current voltage in a liquid crystal display and its evaluation parameters related to liquid crystal and alignment layer materials

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The presence of ionic charges in a liquid crystal layer causes the generation of residual direct current (dc) voltage ($V_{rdc}$) in a liquid crystal cell. $V_{rdc}$ is one of the most important factors governing the image quality of liquid crystal displays, because the existence of $V_{rdc}$ causes the image sticking phenomenon. We studied the generation mechanism of $V_{rdc}$ based on a model of the adsorption and desorption of the ionic charges at the interface between the liquid crystal and alignment layer. In this paper, we propose three evaluation parameters, (i) saturated residual dc voltage, (ii) time to reach its saturation state, and (iii) relaxation time during and after applying the external dc voltage, for effective evaluation of liquid crystal and alignment layer materials from the viewpoint of the improvement of the image sticking. © 2007 American Institute of Physics.

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I. INTRODUCTION

Liquid crystal displays (LCDs) have been used in a wide variety of applications such as personal computers, personal digital assistants, and television sets. However, there still remain insufficiently solved problems for the image quality. One of them is the image sticking phenomenon, by which the previous pattern is still visible when the next pattern is addressed.

One of the major causes of the image sticking is the generation of residual direct current (dc) voltage ($V_{rdc}$), which is the dc offset voltage generated inside a liquid crystal cell (LC cell) under application of the external dc offset voltage. $V_{rdc}$ depends on the structure of the LC cell such as symmetrical structure or asymmetrical structure. The asymmetrical structured LC cell such as hybrid alignment nematic mode generates comparably large $V_{rdc}$. The generation of $V_{rdc}$ is related to the distribution of the ionic charges included in a LC layer as an impurity, as illustrated in Fig. 1. It is important to clarify the relation between behavior of the ionic charge and $V_{rdc}$ during and after applying the external dc offset voltage.

Some studies focused on the ionic charges in the LC cell indicate that several types of ionic charges are included even if the concentration is quite small. 2–5 Sawada et al. succeeded in detecting the existence of the ionic charges by permittivity dispersion measurements. They reported that five types of mobile ionic charges were included in 5CB. 2–4 Murakami et al. found that the mobile ionic charges in 5CB were positive through measurements of transient photocurrent. 5 These studies focused on the detection of the ionic charges. Some other studies focused on the behavior of the ionic charges while the external voltage is applied to the LC cell. Yasuda et al. reported a method for determining time constants of the adsorption and desorption processes of the ionic charges at the interface between the LC layer and the electrode or the alignment layer by measuring ac conductivity. 6 Besides this, they found that the desorption process of the adsorbed ionic charge from the surface is governed by the surface energies of alignment layer materials. 7 However, they did not focus on the generation of $V_{rdc}$. On the other hand, Nakazono et al. reported the generation model of $V_{rdc}$ based on an equivalent circuit. 8 In the research, $V_{rdc}$ is explained by two phenomena; one is the interfacial and dipole polarization of the LC and alignment layers, and the...
other is the electric potential of the adsorbed ionic charges on the surface of the alignment layer. However, their proposed model only focused on the relaxation process of $V_{\text{rdc}}$ after removing the external dc offset voltage. They did not discuss the generation process of $V_{\text{rdc}}$ while the external dc offset voltage is applied. Therefore, those studies are insufficient for an accurate determination of $V_{\text{rdc}}$.

Figure 1 shows a conceptual description of the generation mechanism of $V_{\text{rdc}}$. In Fig. 1(a), positive ionic charges are distributed randomly in the LC layer when the external dc offset voltage is not applied to the LC cell, and $V_{\text{rdc}}$ is zero. Once the external dc offset voltage is applied to the LC cell, those ionic charges drift toward the interface between the LC and alignment layers as shown in Fig. 1(b). Finally, the adsorbed ionic charges contribute to the generation of $V_{\text{rdc}}$ as shown in Fig. 1(c).

In this paper, we will report the generation mechanism of $V_{\text{rdc}}$ based on a kinetic analysis of the ionic charges in the symmetrically structured LC cell. Results will lead to the accurate determination of $V_{\text{rdc}}$. Finally, we will propose the parameters affecting the image sticking.

II. GENERATION MECHANISM OF $V_{\text{rdc}}$

The ionic charges in the LC layer drift toward the interface between the LC and alignment layers when the external dc offset voltage is applied to the LC cell, and finally several number of the ionic charges are adsorbed to the interface. Therefore, $V_{\text{rdc}}$ increases with increasing the density of the adsorbed ionic charges. The equation for adsorbing rate of the ionic charges is as follows:

$$\frac{dn_a}{dt} = k_a[n_f - n_a(t)][N - n_a(t)] - k_d n_a(t),$$  \hspace{1cm} (1)

where $n_a(t)$ is the density of the adsorbed ionic charges which contributes to the generation of $V_{\text{rdc}}, N$ is the density of the adsorbed site at the interface, $n_f$ is the density of the free ionic charges existing in the LC layer, and $k_a$ and $k_d$ are the adsorption and desorption rate constants, respectively. Assuming that $n_a(t)$ is much smaller than $n_f$, that is, $n_a(t) \ll n_f$, Eq. (1) can be modified as follows:

$$\frac{dn_a}{dt} = k_a n_f[N - n_a(t)] - k_d n_a(t).$$  \hspace{1cm} (2)

By solving this equation, the following equation is obtained:

$$n_a(t) = \frac{k_a n_f}{k_a n_f + k_d} N \{1 - \exp[-(k_d n_f + k_d)t]\};$$  \hspace{1cm} (3)

The generation process of the adsorbed ionic charges is analyzed with Eq. (3). Here, the relation between $n_a(t)$ and $V_{\text{rdc}}(t)$ is as follows:

$$Q(t) = q n_a(t) = C_{\text{LC}} V_{\text{rdc}}(t),$$  \hspace{1cm} (4)

where $Q(t)$ is the surface electric charge, $q$ is the elementary electric charge, and $C_{\text{LC}}$ is the capacitance of the LC layer. By substituting Eq. (3) to Eq. (4), the following equation is obtained:

$$V_{\text{rdc}}(t) = \left(\frac{q}{C_{\text{LC}}}\right) \frac{k_a n_f}{k_a n_f + k_d} N \{1 - \exp[-(k_d n_f + k_d)t]\}. $$  \hspace{1cm} (5)

When $t$ is much longer, $V_{\text{rdc}}(t)$ becomes as follows:

$$V_{\text{rdc}}(t \to \infty) = \left(\frac{q}{C_{\text{LC}}}\right) \frac{k_a n_f}{k_a n_f + k_d} N \Rightarrow V_{S-\text{rdc}},$$  \hspace{1cm} (6)

where $V_{S-\text{rdc}}$ is the voltage when $V_{\text{rdc}}$ has reached the saturation state (saturated residual dc voltage) while the external dc voltage is applied.

On the contrary, the relaxation process of the ionic charges within the open circuit state after applying the external dc voltage for specific period is as follows:

$$n_a(t) = n_a(0) \exp\left(-\frac{t}{\tau_R}\right),$$  \hspace{1cm} (7)

where $n_a(0)$ is the density of the adsorbed ionic charges just after removing the external dc voltage and it is related to the initial $V_{\text{rdc}}$, and $\tau_R$ is the relaxation time constant. The relaxation process based on the desorption process of the ionic charges is analyzed by applying Eq. (8).

$$V_{\text{rdc}}(t) = \left(\frac{q}{C_{\text{LC}}}\right) n_a(0) \exp\left(-\frac{t}{\tau_R}\right).$$  \hspace{1cm} (8)

By evaluating $V_{\text{rdc}}$, as a function of the elapsed time for and after which the external dc voltage is applied, the adsorption and desorption processes of the ionic charges at the interface is analyzed. $V_{\text{rdc}}$ is measured by a flicker minimization methodology described in the following section.

III. FLICKER MINIMIZATION

For determining $V_{\text{rdc}}$, an optical method, flicker minimization, is useful because the transmittance of the LC cell placed between crossed polarizers varies with varying the applied ac voltage.\cite{9,10} Figure 2(a) shows a typical voltage-
transmittance curve ($V$-$T$ curve) as a function of the applied rectangular ac voltage. In Fig. 2(b), which is a magnification of the $V$-$T$ curve in Fig. 2(a), the transmittance changes gradually around the voltage region of 50% transmittance, 3.4 V. In case of the existence of $V_{\text{rdc}}$, the flicker is detected as shown in Fig. 3(a) when the rectangular ac voltage of 50% transmittance, 3.4 V, is applied to the LC cell. The applied ac voltage wave form is shown in Fig. 3(b). The reason of the flicker appearance is that the voltage applied to the LC layer, not to the LC cell, changes periodically because of the generation of $V_{\text{rdc}}$. Then, by adjusting the applied dc offset voltage suitably, the flicker is minimized as shown in Fig. 4(a). The adjusting dc offset voltage, which is shown in Fig. 4(b), determined the value of $V_{\text{rdc}}$. In the following sections, the values of $V_{\text{rdc}}$ are determined by this method.

IV. COMPARISON OF $V_{\text{RD}}$ WITH ELECTRIC CURRENT

The electric current is generated when the external dc voltage is applied to the LC cell, because the ionic charges begin to move toward the interface. It is important to compare $V_{\text{rdc}}$ and the electric current. Prior to those measurements, we arranged the cell incorporating homogeneously aligned LC cells having 4.9 $\mu$m gap, the liquid crystal material of ZLI-1132 (Merck Corp.) and the alignment layer material of AL-1051 (JSR Corp.). $V_{\text{rdc}}$ were evaluated every 20 min for 2 h. The electric current was monitored with a current amplifier for 1 h. The measurements were performed at 25 °C. The results are shown in Fig. 5(a) just after applying the dc voltage of 5 V. The time profile of the external dc voltage is shown in Fig. 5(b). According to Fig. 5(a), the time dependency of $V_{\text{rdc}}$ is considerably different from that of the electric current. In case of $V_{\text{rdc}}$, it takes almost 4000 s (approximately 67 min) to reach the saturation. On the contrary, it takes only 100 s for the saturation of the electric current, though the steady-state current of 0.3 nA ($0.3 \times 10^{-9}$ A) exists even after the saturation.

As illustrated in Fig. 6, $V_{\text{rdc}}$ is generated depending on the adsorption and desorption of the ionic charges in the LC layer to and from the alignment layer. Therefore, even the
moving distance of the ionic charges near the interface is small, the number of the adsorbed ionic charge varies, and \( V_{\text{rdc}} \) changes. On the other hand, the generation of the electric current originating from the ionic charges depends on both the moving distance and the concentration in the LC layer, but not on the adsorption and desorption processes, as described in Fig. 7. Therefore, the decay of the electric current shown in Fig. 5(a) depends on both the mobility of the ionic charge and the thickness of the LC layer. The decay process as a function of time is obtained as follows:11,12

\[
i_1(t) = q\mu n_j \frac{V_{\text{appdc}}}{d_{\text{LC}}} \exp\left(-\frac{\mu V_{\text{appdc}}}{d_{\text{LC}}^2} t\right),
\]

where \( i_1(t) \) is the electric current of the decay process, \( \mu \) is the mobility of the ionic charge, \( V_{\text{appdc}} \) is the dc voltage applied to the LC cell, and \( d_{\text{LC}} \) is the thickness of the LC layer. Besides this process, in the constant electric current region, the steady-state current is seen in Fig. 5(a) and expressed as follows:

\[
i_2 = \sigma(V_{\text{appdc}} - V_{\text{rdc}} - \alpha),
\]

where \( i_2 \) is the steady-state current \( \sigma \) is the constant value related to the conductivity of the LC layer, and \( \alpha \) is the threshold voltage where carriers start to flow. The electric current obtained by applying the dc voltage is as follows:

\[
I(t) = i_1(t) + i_2.
\]

As \( V_{\text{rdc}} \) is determined by the optical method, the flicker minimization, it directly relates to the image quality of LCD. Consequently, we propose to evaluate \( V_{\text{rdc}} \) instead of the electric current for the development of the LC and alignment layer materials.

**V. COMPARISON OF \( V_{\text{rdc}} \) WITH AND WITHOUT THE AC VOLTAGE**

In the previous section, the dc voltage having no ac component was applied to the LC cell as the external dc voltage. However, in an actual LCD, \( V_{\text{rdc}} \) is generated during application of the rectangular ac voltage including the dc offset voltage. Therefore, it is important to compare \( V_{\text{rdc}} \) during application of the external dc voltage with and without the ac voltage. The results are shown in Fig. 8(a). The time profile of the externally applied voltage with the ac component is shown in Fig. 8(b). The ac voltage was kept at 30 Hz and 3.4 V, and the dc offset voltage was 5 V. The time profile of the externally applied voltage to the LC cell without the ac component is the same profile that is shown in Fig. 5(b).

According to Fig. 8(a), the time dependency of the values of \( V_{\text{rdc}} \) with and without the ac voltage is almost at the same level with each other. This result indicates that \( V_{\text{rdc}} \) closely depends on the value of the applied dc voltage, but not on the ac voltage. Therefore, in the following section, the external voltages applied to the LC cell were set to the fixed value of 3.4 V, 30 Hz for the ac voltage, and variable for dc offset voltage.

**VI. \( V_{\text{rdc}} \) FROM DIFFERENT EXTERNAL DC VOLTAGES WITH CONSTANT AC VOLTAGE**

We evaluated \( V_{\text{rdc}} \) as a function of the elapsed time of applying various external dc offset voltages at 25 °C. The external dc offset voltages were set at the range from 1 to 5 V with the ac voltage of 3.4 V at 30 Hz. Experimental results are shown in Fig. 9. The fitting results based on Eq. (5) are also shown. According to Fig. 9, the fitting curves fit

**FIG. 7.** Conceptual description of the generation of electric current; the ionic charges drift toward the interface by applying external dc voltage.

**FIG. 8.** \( V_{\text{rdc}} \) as a function of elapsed time of applying dc offset voltage (5 V) with and without ac voltage (30 Hz, 3.4 V) at 25 °C, and (b) time profile of the external voltage with rectangular ac and dc offset voltages.

**FIG. 9.** \( V_{\text{rdc}} \) as a function of elapsed time of applying dc offset voltage with rectangular ac voltage at 25 °C; dc offset voltage: 1–5 V, ac voltage: 30 Hz and 3.4 V.
well with the experimental results in this range of external dc offset voltages. The fact indicates that our proposed model expressed in Eq. (5) is reasonable.

The saturated residual dc voltage \(V_{\text{S-rdc}}\) and the adsorption and desorption rate constants \((k_a, n_f\) and \(k_d)\), which are determined from the fittings, are shown as functions of the external dc offset voltage in Figs. 10 and 11, respectively. According to Fig. 10, \(V_{\text{S-rdc}}\) increases linearly with increasing the external dc offset voltage from 1 to 5 V. On the contrary, according to Fig. 11, both \(k_a, n_f\) and \(k_d\) slightly decrease in this range of the external dc offset voltage, respectively. In the actual LCD, the evaluations of \(V_{\text{S-rdc}}\) and \(k_a, n_f + k_d\), the time to reach its saturation level, are important, because \(V_{\text{S-rdc}}\) directly relates to the final level of the image sticking, and \(k_a, n_f + k_d\) indicates the time to reach the worst image sticking level. These two parameters are crucially effective as the design parameters of the LC and alignment layer materials for LCD fabrications. In particular, to improve the image sticking of LCD, we have to decrease \(V_{\text{S-rdc}}\). Therefore, it is crucially important to evaluate the slope obtained by the relation between \(V_{\text{S-rdc}}\) and the external dc offset voltage shown in Fig. 10.

It is considered that the molecular structure, alignment, or polarizability of the LC and alignment layer materials affect \(k_a\) and \(k_d\).

VII. RELAXATION PROCESS OF \(V_{\text{RDC}}\) AFTER APPLICATION OF THE EXTERNAL DC VOLTAGE

The relaxation process of \(V_{\text{Rdc}}\) was measured after applying the external dc offset of 5 V with the ac voltage of 3.4 V at 30 Hz for 90 min. at 25 °C. (It was carried out in the open circuit state, after applying the external dc offset voltage for 2 h.) The values of \(V_{\text{Rdc}}\) are shown as a function of time for the open circuit in Fig. 12. We compare the experimental result with the theoretical result derived from Eq. (8). The theoretical result is not fitted well with the experimental result, as shown in Fig. 12. Therefore, we extend Eq. (8) to Eq. (12) by assuming that two decay components exist.

\[
V_{\text{Rdc}}(t) = \left( \frac{q}{C_L} \right) n_0(0) \left[ A \exp\left( -\frac{t}{\tau_{R1}} \right) + (1 - A) \exp\left( -\frac{t}{\tau_{R2}} \right) \right].
\]

where \(A\) is the fraction of the component of \(\tau_{R1}, \tau_{R1}\) is the relaxation time constant of the fast relaxation component, and \(\tau_{R2}\) is the relaxation time constant of the slow relaxation component. The theoretical result derived from Eq. (12) is well fitted with the experimental result. This indicates that two relaxation processes of the adsorbed ionic charges exist.

We predict that there are two possibilities for this reason. One possibility is that two different types of ionic charges are included in the LC layer, and this postulation is described by Seiberle and Schadt from their evaluation of voltage holding ratio.\(^{13}\) The other possibility is that two adsorption sites exist at the interface between the LC and alignment layer. The relaxation time during the open circuit state after applying the external dc voltage is also the effective parameter for the development of the LC and alignment layer materials.

VIII. CONCLUSION

The relation between the generation of the residual dc voltage \(V_{\text{Rdc}}\) and the behavior of the ionic charges in the LC layer was clarified based on the kinetic analysis. The generation of \(V_{\text{Rdc}}\) depends on the adsorption and desorption of the ionic charges at the interface between the LC and alignment layers. On the other hand, the electric current depends on the movement of the ionic charges in the LC layer. To develop LCD, the evaluation of \(V_{\text{Rdc}}\), obtained by the flicker minimization, is crucially important because \(V_{\text{Rdc}}\) affects the optical performance of LCD such as the image sticking.

Two parameters, the saturated residual dc voltage \(V_{\text{S-rdc}}\) and the time to reach the saturation state, are proposed as the effective evaluation parameters to develop LC and alignment layer materials of LCD. Besides these two parameters, the relaxation time during the open circuit state after applying the external dc voltage is also the effective
parameter. Those three parameters are obtained by the theoretical calculations of the $V_{dc}$ measurements.

$V_{S-rdc}$ is closely related to the image sticking phenomenon. Therefore, the determination of $V_{S-rdc}$ is the most important and quite effective way for the design of both the LC and alignment layer materials to improve the image quality of LCD.

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