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Guest-Host Type Liquid Crystal Displays

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Guest-Host Type Liquid Crystal Displays†

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Eight modes of the guest-host cells (GH-cells), in which types of dye, liquid crystal and their alignments are adequately combined, are surveyed, and the color contrast of each mode is calculated.

Three modes among them are of positive type display, that is, colored patterns on the colorless background contrary to the initially proposed fundamental GH-cell. Another three modes are the GH-cells without polarizer, by which bright display can be obtained.

Light stability of dyes are also discussed and lifetimes of various dyes are estimated by accelerated life test. As a result, it is found that diazo- and axomethine-dyes without thiazole group as well as anthraqunone-dyes have satisfying lifetimes as long as they are used indoors.

1 INTRODUCTION

Twisted nematic liquid crystal display devices are increasingly being used in portable instruments such as watches, electronic calculators and others. Along with the expansion of their application, however, their narrow viewing angle and their relatively dark display become problematic. As a solution of this problem, the guest–host liquid crystal display devices that make use of dichroic dyes attract special interest.

In this paper, the fundamental behavior of the guest–host cell is explained in the first place, and then various types of the guest–host cells are compared. Finally, the light-stability or light-durability of the dichroic dyes are discussed. Hereafter, the guest–host cell is referred as GH-cell.

† Invited lecture, presented at the Eighth International Liquid Crystal Conference, Kyoto (Japan), June 30–July 4, 1980.

2 FUNDAMENTAL BEHAVIOR OF THE GH-CELL

When rod-like dichroic molecules are doped in liquid crystal, they tend to align parallel to the liquid crystal molecules. In actual practice, however, the direction of dye molecules as well as liquid crystal molecules deviate from the direction of the director as shown in Figure 1 because of thermal fluctuation. If we denote the deviated angle of each dye molecule by α, the order parameter S can be expressed by the average of $\cos^2 \alpha$ as

$$S = \frac{(2\langle \cos^2 \alpha \rangle + 1)}{3}. \tag{1}$$

Here, let β be the angle between the directions of transition moment **C** and of the molecular axis **B**, and ψ the angle between director **A** and the direction of electric field of the incident polarized light **D** (hereafter, abbreviated as polarized direction). Then, absorbances A as a function of β and ψ is represented by[1]

$$A(\beta, \psi) = K_M cd\{(S/2)\sin^2 \beta + (1 - S)/3 + (S/2)(2 - 3\sin^2 \beta)\cos^2 \psi\}, \tag{2}$$

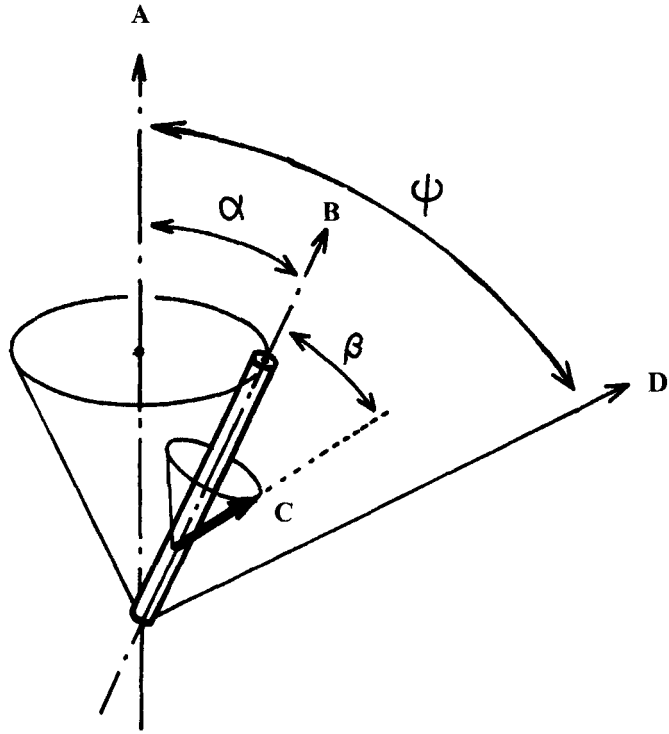


FIGURE 1 Geometrical relationship of directions of **A**: director, **B**: molecular axis of dye, **C**: transition moment and **D**: electric vector of polarized light.

where K_M is a coefficient relating to magnitude of the transition moment and d is the thickness of the mixture of the dye and liquid crystal.

The dichroic dye usually has a transition moment almost parallel to its molecular axis as shown in Figure 2(a). We call this kind of dye as the positive dichroic dye and abbreviated as the p-type dye. This type absorbs a polarized light component $L_{\parallel}$ whose polarized direction is parallel to the molecular axis. Let $A_{\parallel}$ and $A_{\perp}$ be absorbances of the dye in a liquid crystal for the polarized lights whose polarized directions are parallel and perpendicular to the director, respectively. According to Eq. (2), these values for the p-type dye is given by

$$A_{\parallel} = A(\beta = 0, \psi = 0) = K_M cd(1 + 2S)/3 \tag{3}$$

$$A_{\perp} = A(\beta = 0, \psi = \pi/2) = K_M cd(1 - S)/3, \tag{4}$$

where the direction of transition moment is assumed to be completely parallel to the molecular axis. On the other hand, the negative dichroic dye (n-type dye) has been reported lately.[2] This dye has a transition moment almost perpendicular to its molecular axis but its direction of the moment rotates as shown in Figure 2(b) in a nematic liquid crystal, because the nematic state has freedom in rotation. Therefore, the dye absorbs the perpendicularly polarized light.

According to Eq. (2), $A_{\parallel}$ and $A_{\perp}$ for the n-type dye are represented by

$$A_{\parallel} = A(\beta = \pi/2, \psi = 0) = K_M cd(1 - S)/3 \tag{5}$$

$$A_{\perp} = A(\beta = \pi/2, \psi = \pi/2) = K_M cd(2 + S)/6, \tag{6}$$

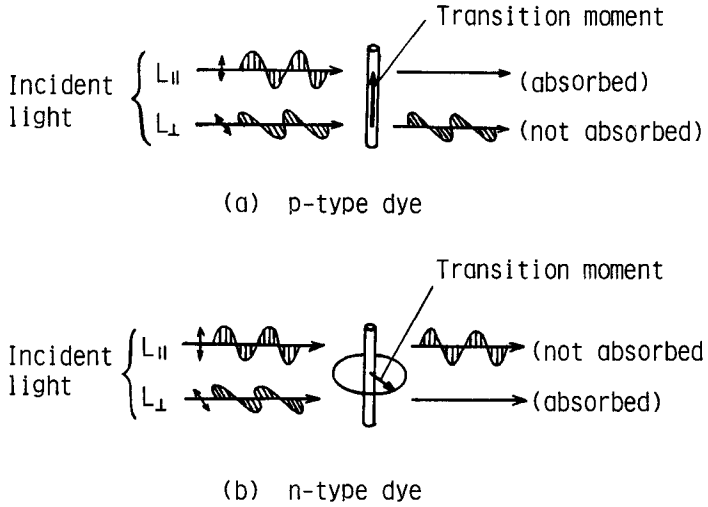


FIGURE 2 Absorbing characteristics of the p-type and the n-type dyes.

where the direction of transition moment is assumed to make at a right angle with the molecular axis.

When a voltage is applied to a mixture of these dyes and liquid crystal, the molecular orientational direction changes, and therefore light absorbing characteristic changes, hence, color switching is possible.

Figure 3 shows the initially proposed fundamental GH-cell.[3] A *p*-type dye and a nematic liquid crystal with positive dielectric anisotropy (referred to as Np-liquid crystal) are used in this cell. The polarized light component $L_\perp$ is removed by a polarizer because $L_\perp$ component is not absorbed by the dye at either off- or on-states. For the component $L_\parallel$, absorbance at maximum absorption wavelength λ_m at off-state is denoted by A_{off}, and that of on-state of sufficiently high voltage is denoted by A_{on}. The absorbances A_{off} and A_{on} can be written as

$$A_{off} = A_\parallel = k_\parallel cd \tag{7}$$

$$A_{on} = A_\perp = k_\perp cd, \tag{8}$$

where $k_\parallel$ and $k_\perp$ are principal absorption coefficients and are, according to

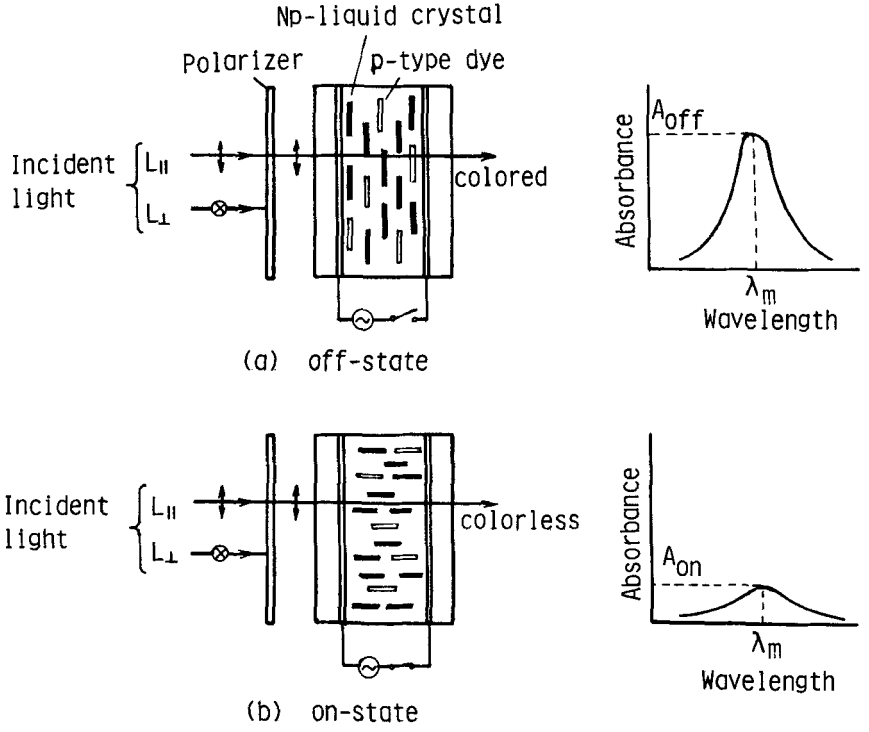


FIGURE 3 The initially proposed fundamental GH-cell.

Eqs. (3) and (4), written as

$$k_{\parallel} = K_M(1 + 2S)/3 \tag{9}$$

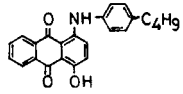
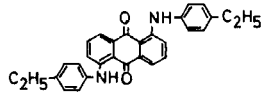
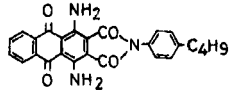
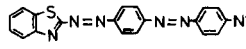
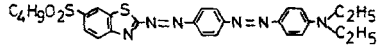
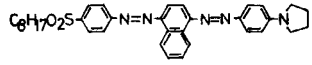
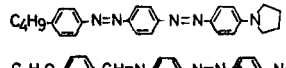
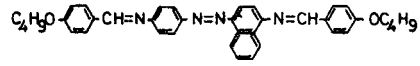
$$k_{\perp} = K_M(1 - S)/3. \tag{10}$$

As a measure of color switching, it is convenient to take the ratio of A_{off}/A_{on}, because this value is equal to the dichroic ratio of the p-type dye, $D_p (= A_{\parallel}/A_{\perp} = k_{\parallel}/k_{\perp})$, in this fundamental cell, and is independent of the dye concentration and the thickness of the liquid crystal layer. Therefore we call A_{off}/A_{on} the color contrast. The value of this color contrast depends both on the order parameter of the host liquid crystal and on the molecular structure of the dye. Therefore, a biphenyl mixture GR–41 is generally used as a host in our experiment.

Table I shows some of the typical dichroic dyes. Nos. 1 and 2 are anthraquinone-dyes reported by Constant *et al.*[6] Their dichroic ratio are not large

TABLE I

Typical dichroic dyes and their properties in the liquid crystal biphenyl mixture GR-41

No.	Dye	Molecular structure	λ_m (nm)	Color	Dichroic ratio
1.	D5		590	Blue	5.3
2.	D35		553	Violet	6.5
3.	G209		687	Blue	9.5
4.	G168		574	Blue	10.6
5.	G165		595	Blue	10.3
6.	G224		574	Bluish Violet	9.7
7.	G205		507	Red	11.4
8.	G232		450	Yellow	12.1

enough but they are known to be light stable, or light durable, as will be mentioned later. Nos. 3 ~ 8 were synthesized by our co-worker, Nippon-Kankoh-Shikiso Laboratory. No. 3 is a kind of anthraquinone dye but with a large dichroic ratio. The others are diazo- and azomethin-dyes. Schadt[7] has presented another kind of anthraquinone dye as shown in Figure 4, recently, the dichroic ratio and stability of which are reported to be promising.

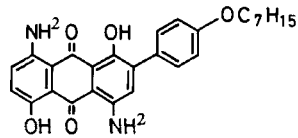


FIGURE 4 Molecular structure of the anthraquinone-dye proposed by Schadt.[7]

3 GH-CELLS WITH POSITIVE TYPE DISPLAY

The fundamental GH-cell mentioned above displays colorless patterns on the colored background, the so called negative type display. But the positive type display is more often required. There are three methods to realize this.

Figure 5 shows one of the methods to realize the positive display.[8] In this

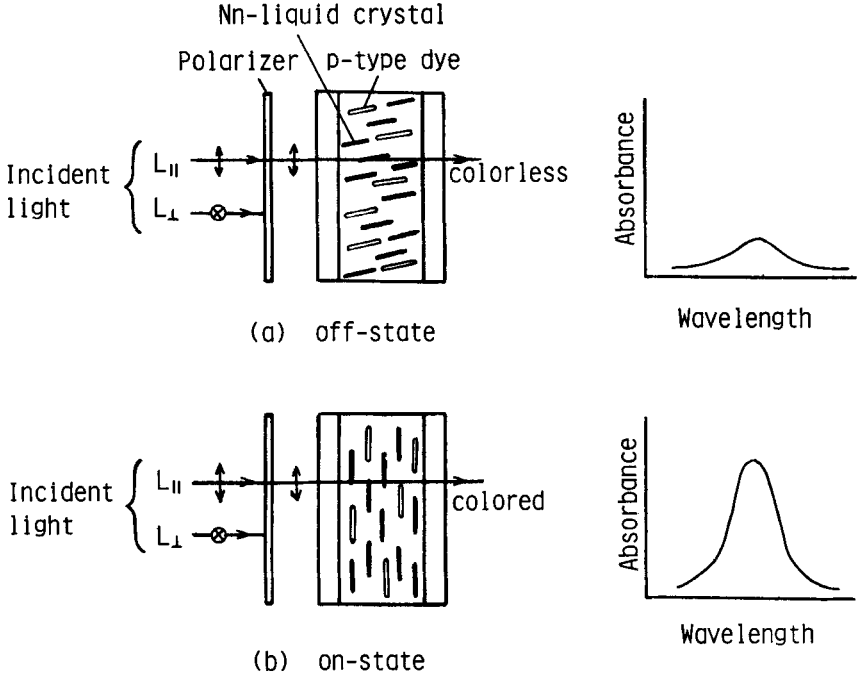


FIGURE 5 The positive type GH-cell using an Nn-liquid crystal.

cell liquid crystal with negative dielectric anisotropy (Nn-liquid crystal) is aligned with a small tilt away from the perpendicular to the substrate. Hence, it is colorless at off-state. At on-state, molecules rearrange themselves parallel to the substrate and therefore the cell becomes colored. The tilted homeotropic alignment can be obtained by an oblique evaporation of SiO followed by treatment with homeotropic surface coupling agent, N,N-dimethyl-N-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP). The tilt angle can be controlled by evaporation angle and thickness of SiO as shown in Figure 6.[9] Tilt angle of 3 to 5 degrees is most suitable for this cell. The color contrast of this cell is written as

$$A_{on}/A_{off} = k_{\parallel}/\{k_{\perp} + (k_{\parallel} - k_{\perp}) \sin^2 \theta\}, \tag{11}$$

where θ is tilt angle. When $\theta = 3 \sim 5$ degrees, the second term in the denominator can be neglected. Figure 7(a) shows the positive type GH-cell of the reflective mode compared with the conventional negative type cell. Both cells can be driven by a voltage as low as 3 V (Figure 7(b)), because liquid crystals with large dielectric anisotropy of -5.9 and $+14.2$, respectively, are used.

Figure 8 shows the second method to obtain the positive type display. In this cell, the Np-liquid crystal and the *n*-type dye are used. The color contrast is rewritten as

$$A_{on}/A_{off} = A_{\perp}/A_{\parallel} = D_n. \tag{12}$$

The problem of this cell is in the difficulty in obtaining high color contrast, because the transition moment of the dye rotates around the molecular axis. According to Eqs. (3) $\sim$ (6), the dichroic ratios of the *n*-type and *p*-type dyes, D_n and D_p, are respectively, expressed by their order parameters, S_n and S_p, as

$$D_n = \frac{A_{\perp}}{A_{\parallel}} = \frac{(2 + S_n)}{2(1 - S_n)} \tag{13}$$

$$D_p = \frac{A_{\parallel}}{A_{\perp}} = \frac{(1 + 2S_p)}{(1 - S_p)}. \tag{14}$$

If $S_n = S_p$, Eqs. (13) and (14) give

$$D_n = \frac{(D_p + 1)}{2}. \tag{15}$$

This indicates that the dichroic ratio of the *n*-type dye is about a half of that of the *p*-type dye. Demus *et al.*[2] have reported this kind of dye with relatively large dichroic ratio, the tetrazine-dye (Figure 9). It is available from Chisso Corporation by the name of GR–63w, whose dichroic ratio is about 5. At

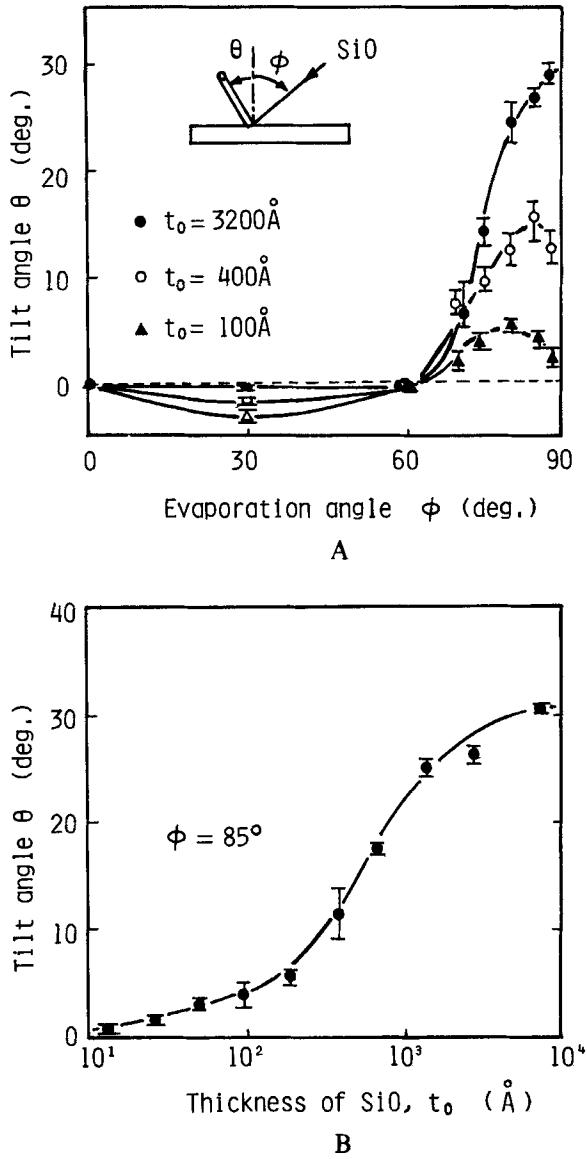
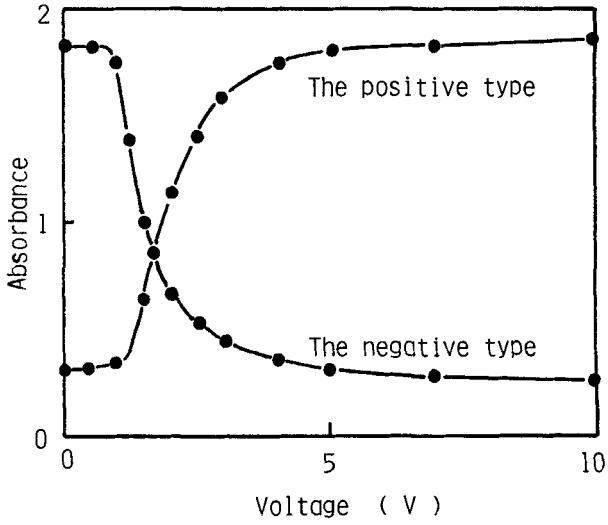


FIGURE 6 Dependences of the tilt angle off normal on the evaporation angle and the thickness of SiO, where the thickness t_0 is defined by normally incident thickness.

present, displayed color of this kind of dye is restricted to purple. Schadt[10] has reported recently a similar dye.

Figure 10 shows the third method to obtain the positive display. This cell

(a)



(b)

FIGURE 7 The positive and the negative type GH-cells

Type	Liquid crystal	$\Delta\varepsilon$	Dye	λ_m	Thickness	Tilt angle
positive	EN-18*	−5.9	G165 (1.0 wt %)	582 nm	12 μm	~3°
negative	GR-41*	+14.2	G165 (1.0 wt %)	595 nm	12 μm	—

* purchased from Chisso Corp.

uses the usual *p*-type dye and the Np-liquid crystal, but requires special surface alignment, that is, homogeneous alignment for colored pattern and homeotropic alignment for colorless background. Therefore, the colored

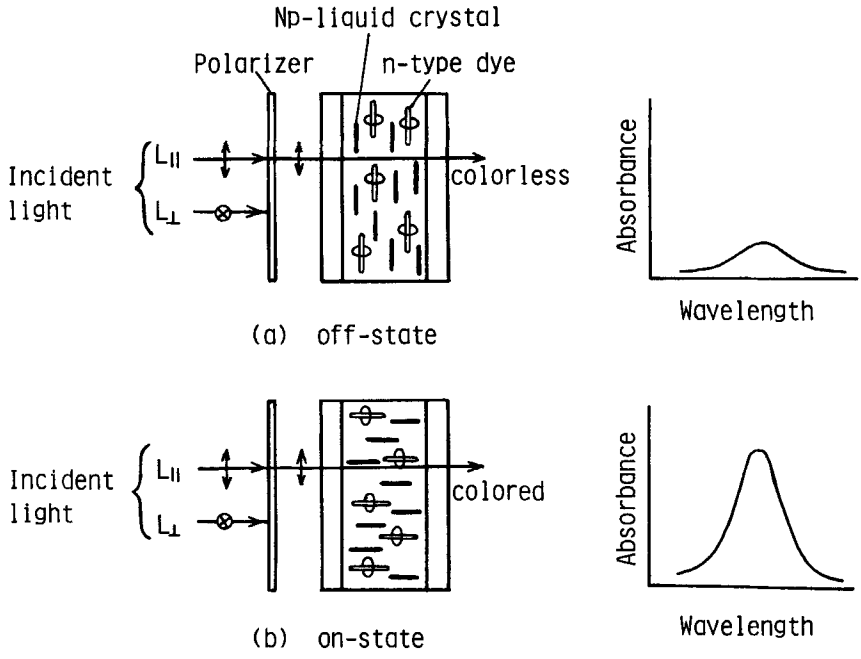


FIGURE 8 The positive type GH-cell using a *n*-type dye.

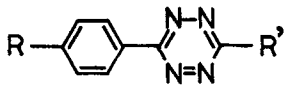


FIGURE 9 Structure of tetrazine-dye.

pattern can be seen at off-state and is erased at on-state. Thus, we call this the quasi-positive type display. This kind of molecular alignment can be modified as shown in Figure 11(a) or (b). The advantage of the modified cell lies in the fact that special surface alignment is necessary only on the left-hand side substrate. The right-hand side substrate is treated as usual as the homogeneous alignment. We actually fabricated this quasi-positive type cell with the alignment of Figure 11(b). The homogeneous alignment was realized by coating with poly-vinylalcohol followed by unidirectional rubbing. The homeotropic alignment was obtained by very thin aluminum layer (typical thickness is about 50 Å) evaporated on the poly-vinylalcohol coat. The aluminum layer changed into transparent alumina in the air, over which Np liquid crystal of biphenyl mixture aligned homeotropically. A sample of the quasi-positive type cell is shown in Figure 12.

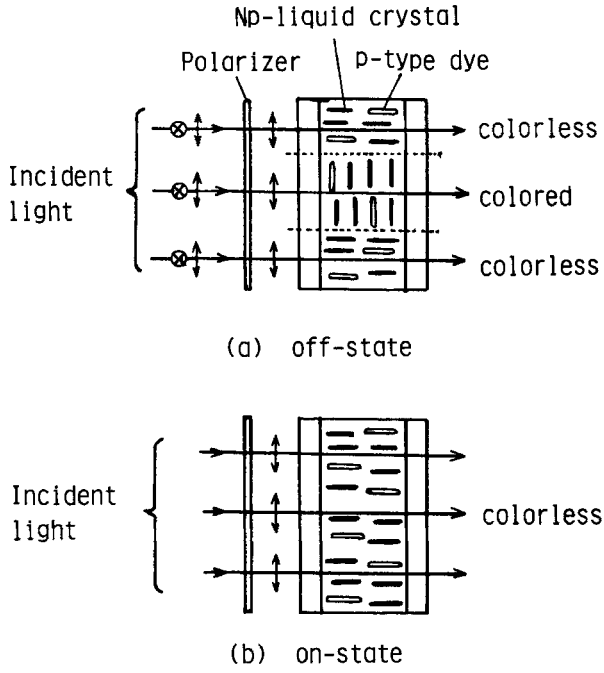


FIGURE 10 The quasi-positive type GH-cell.

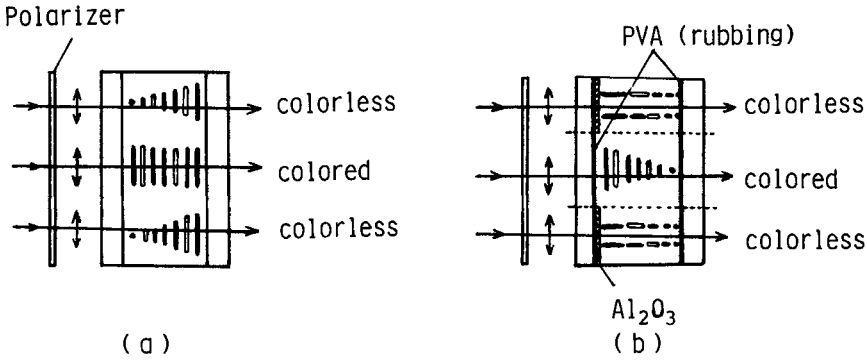


FIGURE 11 The quasi-positive type GH-cells with modified alignments.

4 GH-CELLS WITHOUT POLARIZER

Now, GH-cells mentioned above require one polarizer, so that they have the following two problems.

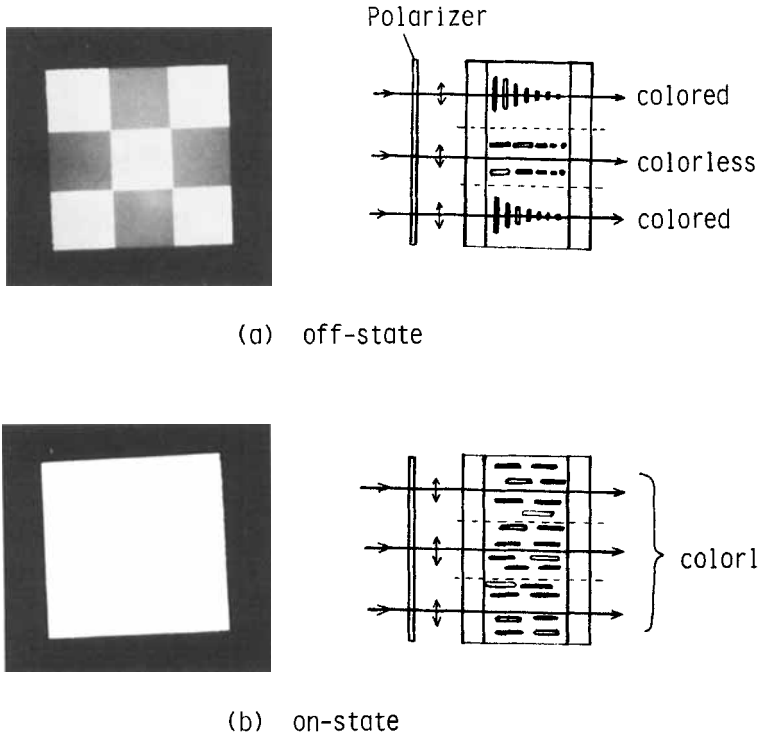


FIGURE 12 Photographs and molecular alignments of the quasi-positive type GH-cell (liquid crystal: GR–41, dye: G165).

1) 50% of the incident light is lost and hence display becomes as dark as the twisted nematic cell.

2) A non-depolarized reflector such as polished metal film should be used, but usually they do not have a wide reflecting angle.

Merely to remove the polarizer from the GH-cells, however, does not lead to a real solution of the problems, because the color contrast becomes poor. There are three GH-cells proposed to solve these problems. These are a GH-cell with a quater wave plate proposed by Cole and Kashnow,[11] a phase change type GH-cell proposed by White and Taylor[12] and a double layered cell suggested by the authors.[13]

The GH-cell with a quater wave plate is used only as a reflective type as shown in Figure 13. At off-state, two polarized components of the incident light change their polarized direction by 90 degrees at their return path. Therefore, both components are absorbed either at the forth or the return path. Assuming that the reflective light is not depolarized and the reflective

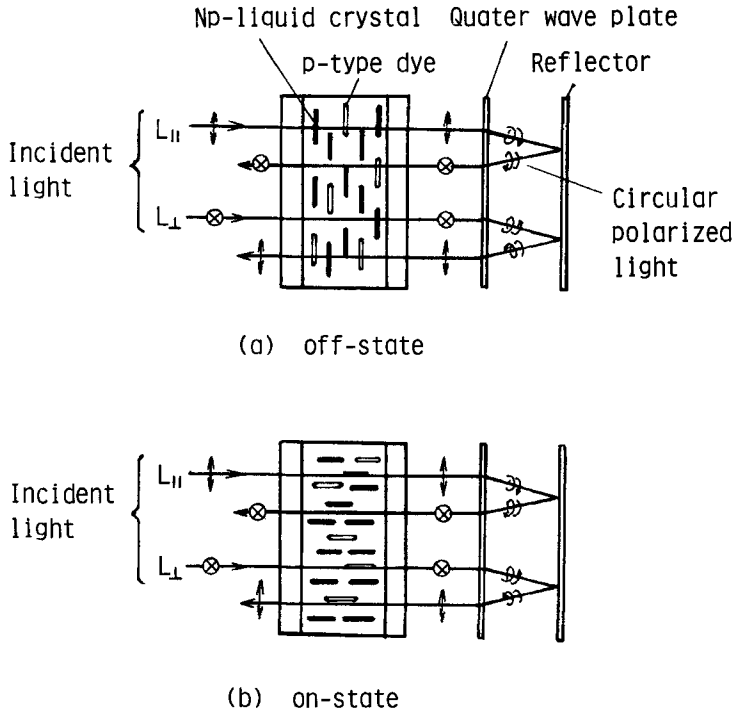


FIGURE 13 The GH-cell with a quater wave plate.

loss is neglected, the color contrast of this cell can be written as

$$\frac{A_{on}}{A_{off}} = \frac{(k_{\parallel} + k_{\perp})cd}{2k_{\perp}cd} = \frac{(D_p + 1)}{2}. \tag{16}$$

The problem of this cell is that it loses the characteristic of a wide viewing angle because the viewing angle of the wave plate itself is not wide enough.

The phase change type GH-cell[12] utilizes voltage induced cholesteric-nematic phase change of cholesteric-Np-liquid crystal mixture doped with a *p*-type dye. The critical voltage of the phase change is denoted by V_{CN}. In this cell, the homeotropic surface treatment is adopted to obtain relatively fast relaxation from nematic state to transparent cholesteric state.

This cell exhibits a two step change in the electro-optical curve as shown in Figure 14. Molecular alignments at ① ~ ③ states are shown in Figure 15(a) ~ (c). The alignment of (a) was first suggested by Kogure *et al.*[14] for a memory cell. This alignment disagrees with the model of random distribution of the helical axis proposed by White and Taylor.[12]

According to the molecular alignments of Figure 15, absorbances A_1 ~

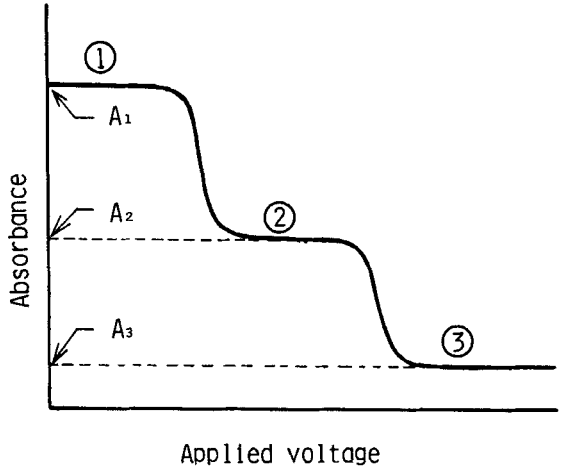


FIGURE 14 Applied voltage dependence of absorbance in the phase change type GH-cell.

A_3 for ① ~ ③ states are represented by

$$A_1 = \log 2 - \log[10^{-c\{k_1(d-2d_s)+2k_\perp d_s\}} + 10^{-c\{k_2(d-2d_s)+2k_\perp d_s\}}] \quad (17)$$

$$A_2 = \log 2 - \log[10^{-c\{(k_\parallel+k_\perp)(d/2-d_s)+2k_\perp d_s\}} + 10^{-ck_\perp d}] \quad (18)$$

$$A_3 = ck_\perp d. \quad (19)$$

Here, Eq. (17) is obtained by modifying the equation proposed by White and Taylor[12] for the planar texture, considering the homeotropic surface layer. k_1 and k_2 in Eqs. (17) and (18) are absorption coefficients for the two modes of traversing light along the helical axis of the cholesteric structure and are written as follows.

$$k_1 = \frac{(n_e^2 k_\parallel + n_0^2 k_\perp \beta_1^2)}{(n_e^2 + n_0^2 \beta_1^2)} \quad (20)$$

$$k_2 = \frac{(n_e^2 k_\parallel + n_0^2 k_\perp \beta_2^2)}{(n_e^2 + n_0^2 \beta_2^2)}, \quad (21)$$

where n_0 and n_e are respectively reflective indicies of ordinary and extra-ordinary light, and β_1 and β_2 are ellipticity for the two modes. d_s in Eqs. (17) and (18) is thickness of the each surface layer. We estimated d_s by measuring the relationship between rotation angle R and thickness of the liquid crystal layer d, which was represented by

$$R = \gamma p(d - 0.4p) \quad (22)$$

for $d/p > 1.2$, where γ was a constant and p was the helical pitch. Eq. (22)

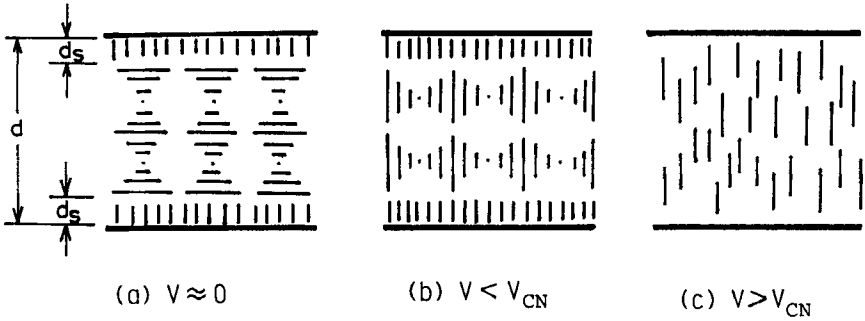


FIGURE 15 Molecular alignments of the phase change type GH-cell.

indicates

$$2d_s = 0.4p. \tag{23}$$

According to Eqs. (17) ~ (21) and (23), A_1/A_3 and A_2/A_3 are calculated as a function of $1/p$ by using physical parameters of the host liquid crystal GR-41 and the guest G 113 as shown in Table II. The result is shown in Figure 16(a) by solid line compared with the experimental values. The broken line in this figure indicates the calculated value without consideration of the homeotropic surface layer for comparison. Figure 16(b) shows the $1/p$ dependence of the phase change voltage V_{CN}. These results are summarized as follows.

1) The calculated curve agrees well with the experimental values as shown in Figure 16(a), so that the molecular alignment of Figure 15 is considered to be reasonable.

2) Switching between ① and ③ states gives higher color contrast. But existance of the middle state ② makes the multiplex driving impossible.

TABLE II

Parameters used in the calculation of the phase change type GH-cell (liquid crystal: GR-41, dye:G113)

Parameter	Value
λ_m	515 nm
$k_{\parallel}$	0.273 (wt %)$^{-1}\cdot(\mu m)^{-1}$
$k_{\perp}$	0.0317 (wt %)$^{-1}\cdot(\mu m)^{-1}$
c	1.20 wt %
d	11.2 μm
n_0 at λ_m	1.51
n_e at λ_m	1.79

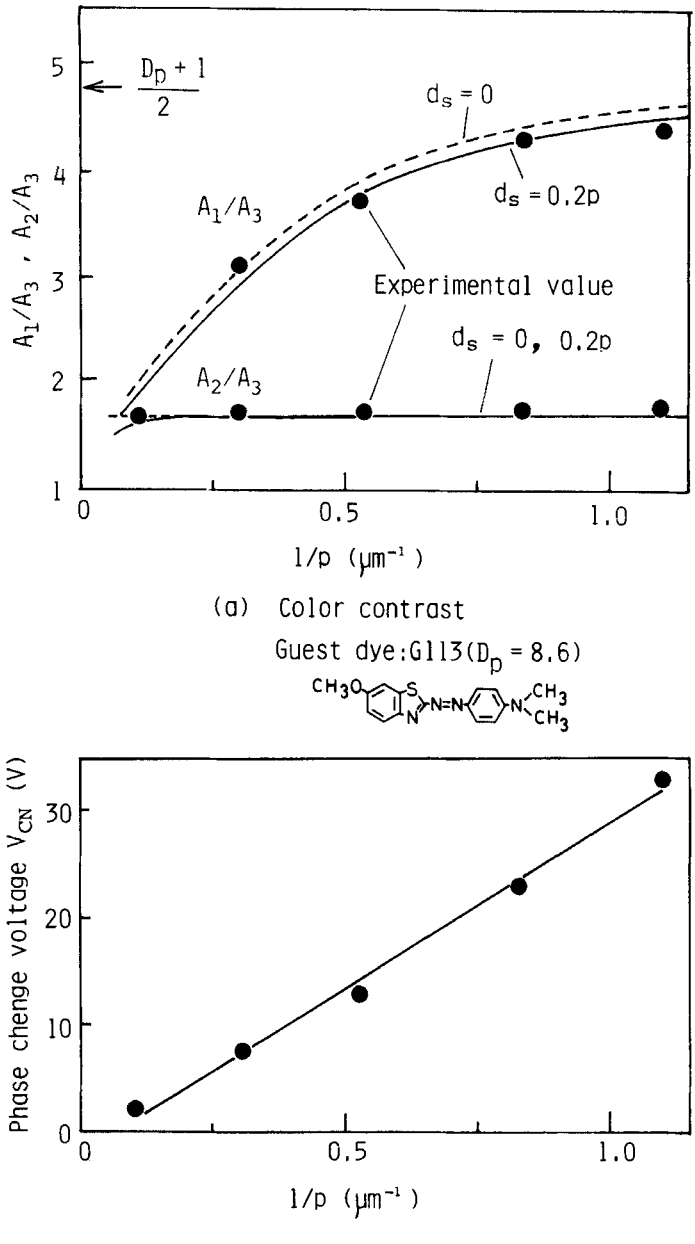


FIGURE 16 Reciprocal pitch $1/p$ dependence of the color contrast A_{off}/A_{on} and the phase change voltage V_{CN} (liquid crystal: GR-41 doped with cholesteryl nonanoate, $d = 11.2\ \mu m$).

3) Absorbance at ③ state increases up to $(D_p + 1)/2$ with increase of d/p, but at the same time V_{CN} increases accordingly. Therefore, high color contrast of the cell requires a high driving voltage, typically $15 \sim 20$ V.

However, this cell has important features, that is, brightness and wide viewing angle in the reflective mode. This is because not only a polarizer can be removed but any depolarizing reflector such as a white paper on a ceramic plate can be used. Therefore, this cell is useful unless low driving voltage and multiplex driving are required.

Figure 17 shows the double layered GH-cell (referred to as DGH-cell).[13] Molecular alignments in two layers are at right angle with each other, so that incident two polarized light components are absorbed at either the first or the second layer at off-state. Absorbances at off- and on-state of this cell are represented by

$$A_{\text{off}} = (k_{\parallel} + k_{\perp})cd \tag{24}$$

$$A_{\text{on}} = 2k_{\perp}cd. \tag{25}$$

Then, the color contrast can be represented by

$$\frac{A_{\text{off}}}{A_{\text{on}}} = \frac{(k_{\parallel}/k_{\perp} + 1)}{2} = \frac{(D_p + 1)}{2}. \tag{26}$$

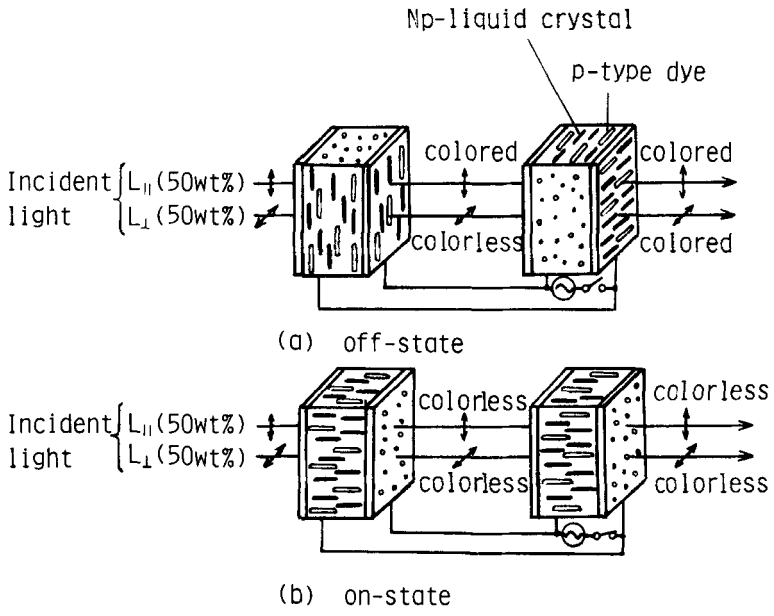


FIGURE 17 The DGH-cell.

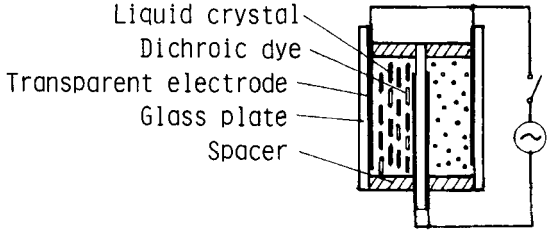


FIGURE 18 Cross section of the DGH-cell.

Figure 18 shows the cross section of an actual DGH-cell. To prevent the display patterns of the two cell layers from shifting from each other when viewed from an oblique direction, the thickness of the central glass plate should be smaller than about 0.7 mm.

The reflective DGH-cell is compared with the usual GH-cell with and without a polarizer in Figure 19. In the DGH-cell, a white paper is used as

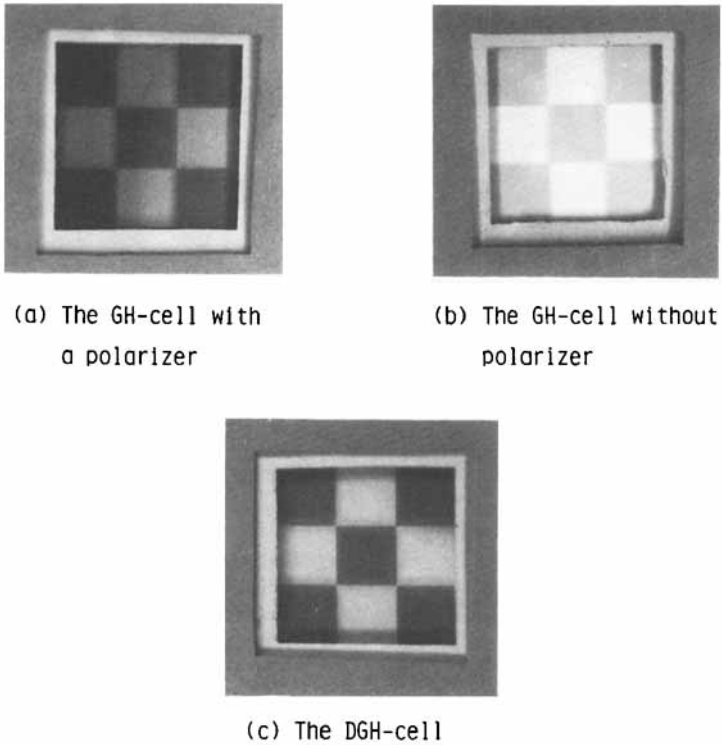


FIGURE 19 Comparison of the GH-cells with and without a polarizer and the DGH-cell (liquid crystal: GR-41, dye: G165).

a reflector, while in the GH-cell, a polished aluminum film is used. It is seen that the DGH-cell exhibits bright and good color contrast.

This kind of DGH-cell is the negative type, while a positive type DGH-cell[13] can also be made by using Nn-liquid crystal as shown in the Figure 20, where the liquid crystal is aligned with a small tilt from the perpendicular in the same manner as the single layer positive type cell mentioned previously. The color contrast can be expressed by neglecting the tilt angle as

$$\frac{A_{on}}{A_{off}} = \frac{(k_{\parallel}/k_{\perp} + 1)}{2} = \frac{(D_p + 1)}{2}. \tag{27}$$

Figure 21(a) shows the positive type DGH-cell compared with the negative type. Either of them is driven by 3 V. Their properties are shown in Figure 21(b).

The patterning technique of surface alignment used in the quasi-positive GH-cell mentioned before, can also be applied to the DGH-cell.

5 COMPARISON OF VARIOUS TYPES OF GH-CELL

Characteristics of various GH-cells stated in this report are summarized in Table III. It is seen that each cell has merits and de-merits and hence they

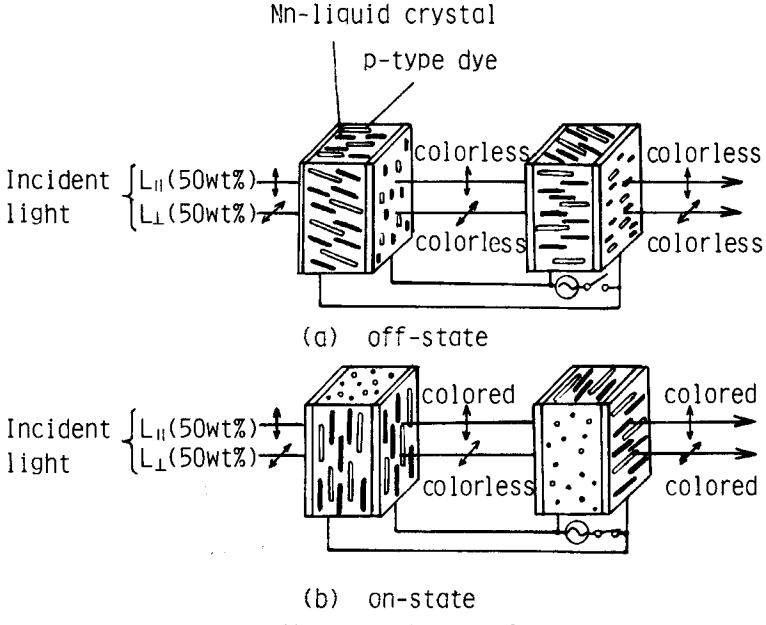
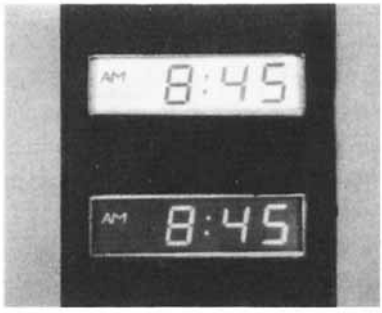
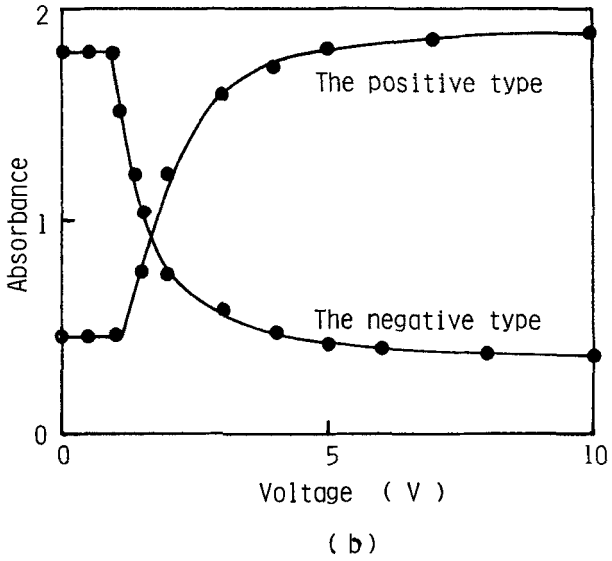


FIGURE 20 The positive type DGH-cell.



(a)



(b)

FIGURE 21 The positive and the negative type DGH-cell.

Type	Liquid crystal	Dye	λ_m	Thickness	Tilt angle
positive	EN-18	G165 (0.84 wt %)	582 nm	12 μm	$\sim 3°$
negative	GR-41	G165 (0.84 wt %)	595 nm	12 μm	—

should be properly applied according to the purposes for which they are used. For example, Nos. 1, 2 and 4 have high color contrast but they are insufficient in brightness. Therefore, they are recommended to be used as a transmissive type rather than reflective type. No. 3 is easy to fabricate as a positive type cell, though brightness, color contrast and the displayed color

TABLE III

Characteristics of various GH-cells

Type	Polarizer	Type of display	Color contrast	Brightness	Viewing angle in reflective mode	Drivine voltage	Easiness of fabrication
1. Original GH-cell	used	nega.	○ (~10)	△	△	~3 V	○
2. GH-cell using a Nn-Lc	used	posi.	○ (~10)	△	△	~3 V	△
3. GH-cell using a *n*-type dye	used	posi.	△ (~5)	△	△	~3 V	○
4. Quasi-positive GH-cell	used	posi.	○ (~10)	△	△	~3 V	△
5. Phase change type GH-cell	no	nega.	△ (~5)	○	○	~15 V	○
6. GH-cell with a $\lambda/4$-plate	no	nega.	△ (~5)	○	△	~3 V	○
7. DGH-cell (double layer)	no	nega.	△ (~5)	○	○	~3 V	△
8. DGH-cell of positive display	no	posi.	△ (~5)	○	○	~3 V	△

○: good, △: inferior.

are restricted. No. 5 is useful as a bright reflective type if a high driving voltage is available. Nos. 7 and 8 are suitable when brightness, wide viewing angle and low driving voltage are required in the reflective mode.

6 LIGHT STABILITY OF DYES

Here, we consider the stability against visible light rather than ultraviolet light because the actual cell is usually protected from UV-light by using a UV-cut filter.

The degradation property is theoretically analyzed.[15] It is considered that the cell is exposed to a light of intensity per unit area of $I(\lambda)$ given as a function of wavelength λ. Let $k(\lambda)$ denote the absorption coefficient and $p(\lambda)$ denote deterioration probability of dye when unit intensity of light of wavelength λ is absorbed, so that degradation rate of the dye can be expressed as follows.

$$-\int_0^d (dc/dt)\,dx = (1/\log e)\int_0^d \int_0^\infty k(\lambda)P(\lambda)I(\lambda)10^{-k(\lambda)cx}cd\lambda\,dx, \quad (28)$$

where x is depth in the liquid crystal layer and d is its whole thickness. Here, let us assume that degradation of the dye is induced by the light of wavelength region of $\lambda_0 \pm \Delta\lambda/2$, and in this region $k(\lambda)$, $p(\lambda)$ and $I(\lambda)$ are constant with respect to λ, so that $k(\lambda) = k(\lambda_0)$, $p(\lambda) = p(\lambda_0)$, $I(\lambda) = I(\lambda_0)$. By practicing the integrals of Eq. (28), the following equation is obtained.

$$k(\lambda)(c - c_0)d + \log\{(1 - 10^{-k(\lambda_0)cd})/(1 - 10^{-k(\lambda_0)c_0d})\} = -\Delta\lambda k(\lambda_0)P(\lambda_0)I(\lambda_0)t, \quad (29)$$

where c_0 is the initial dye concentration. Let A_0 and A denote absorbances at the maximum absorption wavelength λ_m of initial and after irradiation time t, respectively. Then Eq. (29) can be rewritten as follows.

$$\log(10^{Ak(\lambda_0)/k(\lambda_m)} - 1) = \log(10^{A_0k(\lambda_0)/k(\lambda_m)} - 1) - \Delta\lambda k(\lambda_0)P(\lambda_0)I(\lambda_0)t. \quad (30)$$

It was found by numerical analysis that absorbance A decreased almost linearly with time t while the decrease was not large. This relationship agrees with the experimental results as shown in Figure 22 in the range of $A = A_0 \sim 0.8A_0$. Therefore, the lifetime can be calculated by extrapolating the gradient of initial property. Error of the lifetime obtained by this extrapolation is estimated within about 10% if the lifetime is defined as the time when absorbance changes from A_0 to $0.8A_0$. On the other hand, Eq. (30) indicates that the lifetime is inversely proportional to the light intensity if the spectrum distribution of the light source does not change. We have confirmed this relationship experimentally.[15] Therefore, the practical lifetime of the dye can be easily obtained by accelerated life test by using intense light.

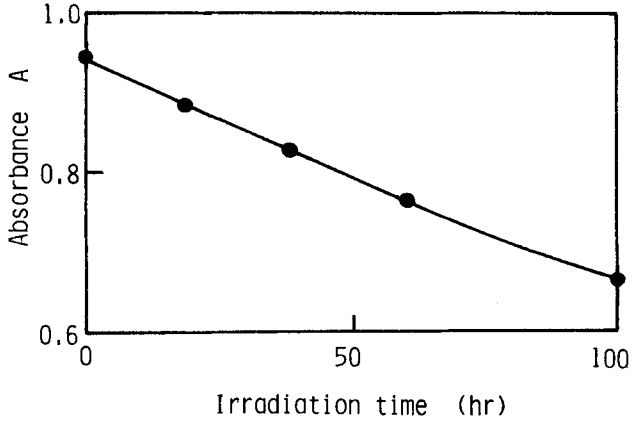


FIGURE 22 Irradiation time dependence of absorbance of the GH-cell at λ_m (liquid crystal: GR-41, dye: G165, light: fluorescent light of 41 000 lx).

Table IV shows the lifetimes of dyes listed in Table I. Here, the accelerated lifetime indicates the experimental value obtained by the method mentioned above by using 41,000 lx light of fluorescent lamps and a UV-cut filter shorter than 395 nm. The calculated lifetime of the transmissive cell indicates the value calculated from the accelerated lifetimes, assuming that the cell is irradiated by a 6 watt fluorescent lamp through a diffuser, a polarizer and the UV-cut filter. The light intensity of this condition was evaluated to be 800 lx. The anthraquinone-dyes of Nos. 1 ~ 3 are superior in light stability, but this kind of dye is difficult in realizing various colors with sufficient color contrast. On the other hand, diazo-dyes of Nos. 4 ~ 8 are easy to realize large dichroic ratio for various colors but Nos. 4 and 5 with thiazole base are

TABLE IV

Lifetimes of the dyes listed in Table I

No.	Dye	Dichroic ratio	Accelerated lifetime (hr)	Calculated lifetime (years)
1.	D5	5.3	5.9×10^3	35
2.	D35	6.5	—[a]	—
3.	G209	9.5	—[a]	—
4.	G168	10.6	3.8×10	0.2
5.	G165	10.3	7.0×10	0.4
6.	G224	9.7	5.3×10^2	3
7.	G205	11.4	2.3×10^3	13
8.	G232	12.1	3.8×10^3	22

Liquid crystal: GR-41.
[a] Almost no change was observed.

inferior in stability. The diazo-dyes without the thiazole base such as Nos. 6 ~ 8, however, have adequate lifetime of about 3 ~ 20 years. This kind of dye is considered feasible practically at present as long as it is used indoors.

7 SUMMARY

Eight GH-cells with various combinations of *p*-type or *n*-type dyes, Np-, Nn- or cholesteric liquid crystals, homogeneous, homeotropic or tilted surface alignments are surveyed, and their characteristics are compared.

GH-cells using a *p*-type dye and a polarizer exhibit high color contrast which is equal to dichroic ratio of the dye but are poor in brightness. On the other hand, bright display with wide viewing angle can be obtained by the phase change type GH-cell and the double layered GH-cell (DGH-cell) though their color contrasts are about a half of the dichroic ratio. The former requires a higher driving voltage and its display is restricted to the negative type, while in the latter mode the driving voltage is as low as 3 V and the positive as well as negative display is available.

Finally, light stability of the dyes was discussed and lifetime was determined as the time required for the absorbance to change from A_0 to $0.8A_0$ estimated under condition of light of 800 lx. The lifetimes of various dyes are estimated by accelerated lifetest. Then, it is found that the anthrazuinone-dyes have lifetime larger than 35 years and that the diazo- and azomethin-dyes without the thiazole group have a lifetime of 3 ~ 20 years. These kinds of dye are considered feasible practically at present as long as they are used indoors. Nevertheless more suitable dyes in terms of stability as well as in dichroic ratio are expected to be developed henceforth.

Acknowledgment

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