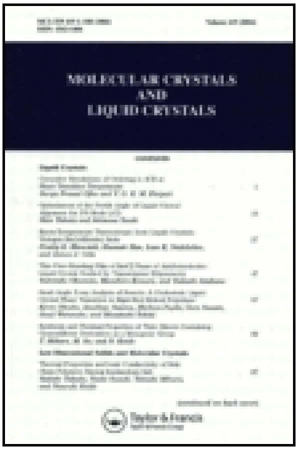

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New Quantitative Method for the Determination of UV Stability in Various LC + DYE Mixtures

T. Véghely [a]

[a] Industrial Research Institute for Electronics, HIKI, Budapest, Hungary

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New Quantitative Method for the Determination of UV Stability in Various LC + DYE Mixtures

T. VÉGHELY

Industrial Research Institute for Electronics, HIKI, Bp. 62. P.O.B. 348, Budapest, Hungary

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The typical forms of degradations in various dye + LC mixtures under increased UV radiation are discussed. The forms of degradation are illustrated by microphotographs. The proposed stability factor (SF) permits a quick quantitative comparison for UV stability. The usefulness of SF is demonstrated with several commercially available dyes and with Di-Triazolo-Benzoate (DTB) derivatives. These DTB derivatives synthesized for our purposes exhibit positive absorption anisotropy, liquid crystalline like behavior above 120°C and high UV stability. By introducing the concept of Stabilizing Influence of Dyes (SID) the interpretation of some interesting effects observed in connection with the UV stability of various mixtures is given.

INTRODUCTION

The idea of producing color switching by mixing dyes with LC materials has been known since the late sixties. Ever since this effect has been discovered, the Guest-Host working mode is being considered as one of the potential rivals to black and white TN working mode. The problems of making appropriate dichroic LCDs are associated with the difficulties of finding dyes with high dichroism (or dichroic ratio), with high solubility in LC materials and with satisfactory UV stability.

Many attempts were carried out to render these partly contradictory requirements consistent with each other in order to improve the performance of dichroic liquid crystal displays (DLCD). It was shown by Constant *et al.*[1] and by many others that to achieve high order parameter and high solubility in the same dye is difficult and sometimes even incompatible. D. L. White and G. N. Taylor[2] demonstrated that DLCDs showing good contrast can be processed without polarizers. Since polarizers act as UV filters, their elimination makes the UV stability requirements for dye + LC mixture more pronounced. In this case the mixture itself must show an acceptable level of stability. Though some dyes with both high order parameter and excellent UV stability were synthesized by the firm BDH, their solubility is rather low (for dye D 16 $C_{max} = 2.2\%$ in E7). In spite of these efforts only a very limited number of dyes proved to meet all of the abovementioned requirements.

The recent investigations of D. Demus *et al.*[3] confirmed our earlier presumption that a possible way of increasing the solubility of dyes is to provide dye with liquid crystalline-like properties. A few years ago Di-Triazolo-Benzoate (DTB) derivatives were synthesized[4] exhibiting liquid crystalline like behavior in the high temperature region above 120°C, showing an intensive redish-yellow color and positive absorption anisotropy ($\Delta\alpha > 0$). In our latest publication[4] several optical properties of one of these DTB derivatives were reported and in the present case we complete our earlier results with UV stability investigations. Further data reporting the UV stability of various LC mixtures are disclosed as well.

SYNTHESIS

Previously F. Muzik and Z. I. Allan[5] investigated the linear Di-Triazolo-Benzoate derivatives to which group our dyes also belong. Their processing method is the following: two mols of diazonium compound are linked with the benzol-sulfonil or tozil derivatives of meta-phenylen-diamin. After hydrolysis the resulting bis-azo derivatives are cyclized. The final product is the 2,6 H-2,6 bis-substituted-di-triazolo-benzoate.

EXPERIMENTAL

At first the solubilities of the DTB derivatives were investigated. We have found that even the longest member of this dye family (DIAMO) shows excellent solubility. A concentration above 10% by weight could be reached easily without recrystallization. The tests were carried out with various LC materials (E7, NP 684, NP 1132, NP 5A, ROTN-101, ROTN-403, ROTN-430).

The absorption measurements were performed with cells made of Corning 7059 glasses. Having evaporated the inner surfaces with SiO at grazing angle of 30° to get parallel orientation, the cells were filled above the N-I transition to achieve better orientation. The nominal thickness between the glasses was 15 μm. The measurements were taken in the visible range between 400 and 700 nm at room temperature, with a spectrophotometer (Spekol, Karl-Zeiss Jena) by inserting a THN polarizer (POLAROID) between the sample and the monochromator. The absorption maximum was in the green. The dichroic ratio ($A_R = A_{\parallel}/A_{\perp}$) as a function of wavelength is shown in Figure 1.

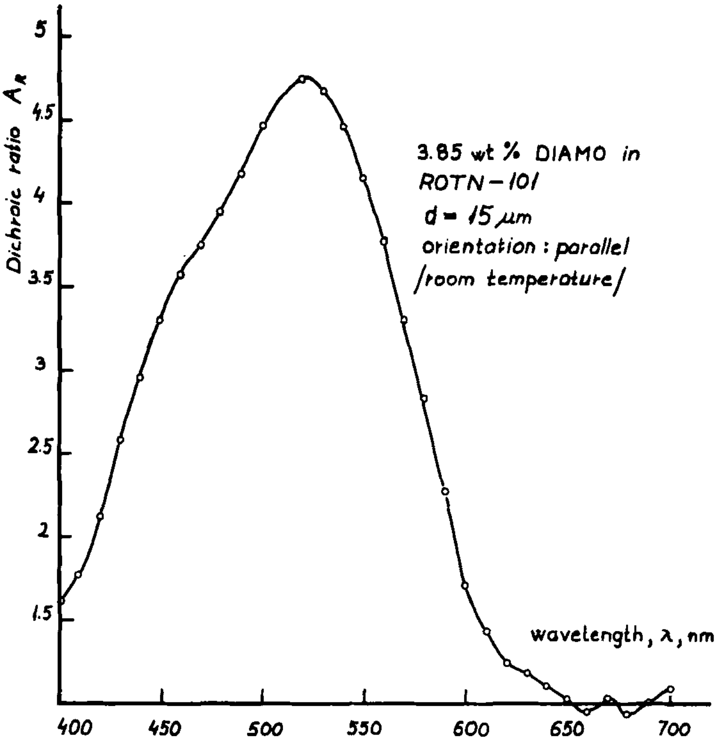

FIGURE 1 The dichroic ratio of DIAMO as a function of wavelength.

For the UV stability tests experimental cells were made. The nominal thicknesses of the cells varied between 10 and 15 μm. As UV source a HgL 250 W (TUNGSRAM) lamp (ϕ = 12 klm) was used. The rate of exposure was minimum 5000 lx (measured with Se-Fe sensor) in the plane of 30 cm distance from the lamp. (We have to note that this is an accelerated examination. An exposure to direct sunlight loads the LCDs less than the exposure to the radiation of this lamp, as it gives a significantly higher amount of energy radiation in the UV region.) The ambient temperature during the tests was 54°C. The samples were exposed to the radiation for approximately 50 hours. We analyzed the changes by visual observations, microphotographs and transmission spectra taken before and after the exposure. A part of each investigated cell was covered with black self-adhesive tape. This protected area served as a reference basis for quick visual comparison between exposed and unexposed areas. The transmission spectra were taken by 10 nms. The tested dyes were dissolved in liquid crystals E7 (BDH) or ROTN-101 (Hoffmann La-Roche).

Preliminary investigations showed that the host material itself might have a contribution to the ageing of the mixture as a whole. Therefore the host materials alone were investigated under the same conditions. In Table I the investigated samples are listed. The quantity of the optically active dopant is given in percent by weight relative to the LC host. The quantity of the dye is also given in percent by weight (or in percent by mol/liter in brackets) relative to the weight of the whole mixture.

DISCUSSION

According to our investigations the stability of the various materials against UV radiation was very different. In most cases we observed a pronounced—in some cases very dramatic—change in color compared with the color of the reference areas. The border line between the exposed and unexposed areas was very sharp in the cases of strong degradation. (Visual and microscopic observations.)

The most dramatic change in color was observed in the case of SUDAN BLACK B, its original blue color was transformed into red.

The ROTN-101 host (with or without CB 15 dopant) showed a medium

TABLE I

The list of mixtures investigated for UV stability.

Dye	*Concentration* %wt	(% mol/liter)	Dopants CB 15 %wt	 C 15 %wt	LC Host
D 35 (BDH)	1.62	(0.038)	—	1	E7
D 16 (BDH)	1.92	(0.042)	—	1	E7
—	—		—	1	E7
DIAMO (VRF)	3.85	(0.085)	—	—	ROTN 101
DIAMO (VRF)	3.85	(0.085)	2	—	ROTN 101
DIAMO	3		3	—	ROTN 101
Sudan Black B.	2				
Forondunkelblau E-2RL (Sandoz)	5.9		1.35	—	ROTN 101
Foronbrillantrot E-RLN (Sandoz)	6.68				
—	—		—	—	ROTN 101
—	—		2	—	ROTN 101
Foronrot E-2GL (Sandoz)	8.29	(0.331)	3	—	ROTN 101
Forondunkelblau E-2RL (fl) (Sandoz)	5.2		2	—	ROTN 101
Foronbrillantrot E-2BL	6.5		—	—	ROTN 101
Forondunkelblau E-2RL	2.7				
Sudan Black B.	2.0	(0.048)	3	—	ROTN 101

level of color change—(colorless changed into yellowish)—and a strong transformation of the nematic state could be detected as the isotropic phase appeared on the exposed areas. The same effect could be observed in some dye + ROTN-101 mixtures, too (for example FORONROT E-2 GL, SUDAN BLACK B.). It was interesting that certain dye + ROTN 101 mixtures exhibited only medium change in color without the appearance of the isotropic phase (DIAMO, FORONDUNKELBLAUE-2RL, DIAMO + SUDAN BLACK B.).

In the case of samples with dyes D 35, D 16, DIAMO, DIAMO + SUDAN BLACK B., FORONDUNKELBLAU E-2RL + FORONBRILLANTROT E-RLN and host E7 + 1% C15 no change in color was observed and only in transmission were any differences detected. The microphotographs taken with crossed polarizers can illustrate the nature of the changes (Figures 2–12; Magnifications approximately 160×).

According to the visual and microscopic observations the ageing of the samples can be attributed to two reasons. One of these is the ageing of the dye (color change), the other one is the degradation of LC host itself.

We also analyzed the samples by investigating the transmission spectra. Several spectra of the above mentioned mixtures were discussed previously.[4]

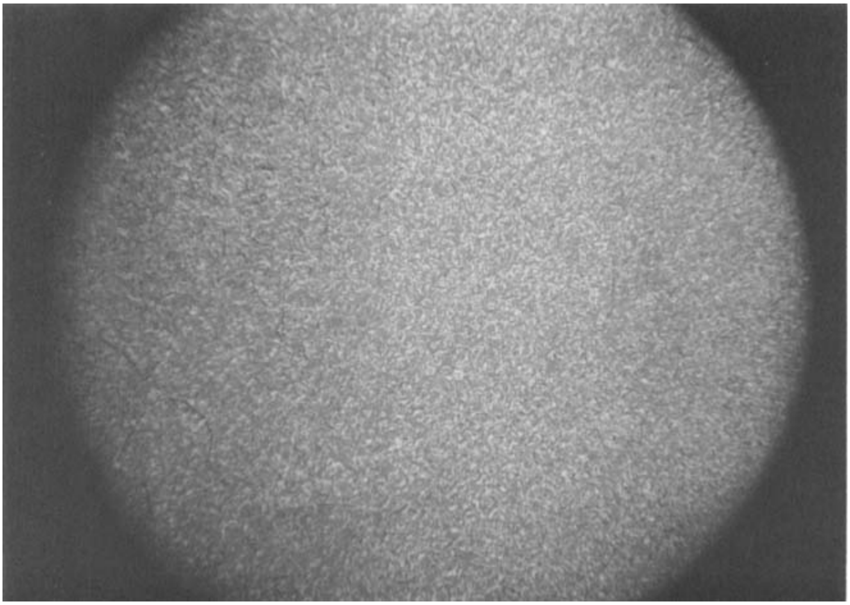

FIGURE 2 Microscopic picture of Sudan Black B, in ROTN-101 Before UV test (Sample No. 13 in Table II).

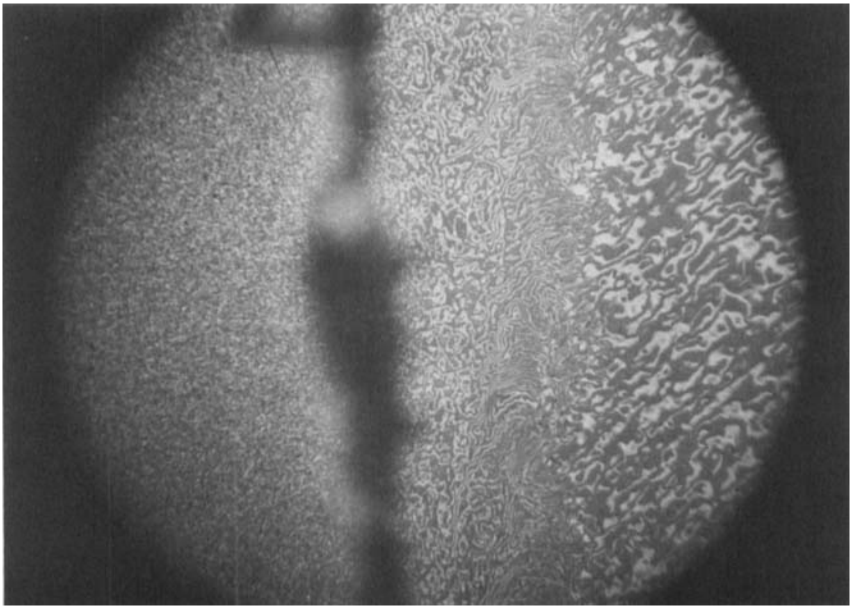

FIGURE 3 As Figure 2; after UV test. Transition area. Left side: unexposed. Right side: exposed to UV.

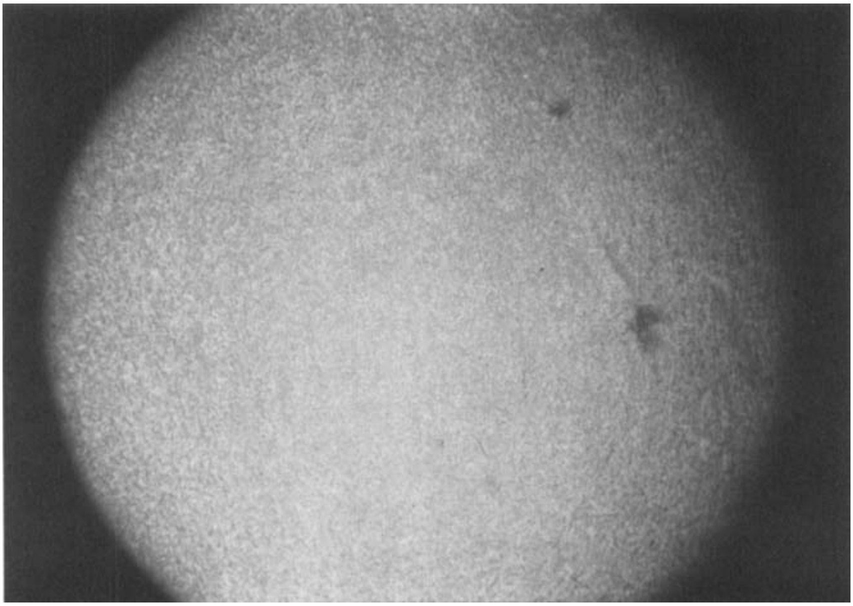

FIGURE 4 Microscopic picture of FORONROT E-2GL in ROTN-101; before UV test (Sample No. 10 in Table II).

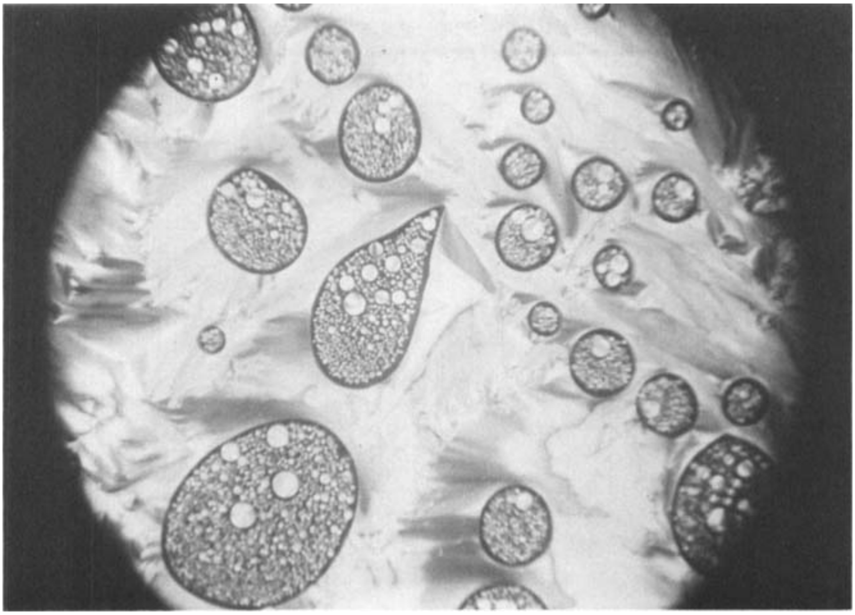

FIGURE 5 As Figure 4; after UV test.

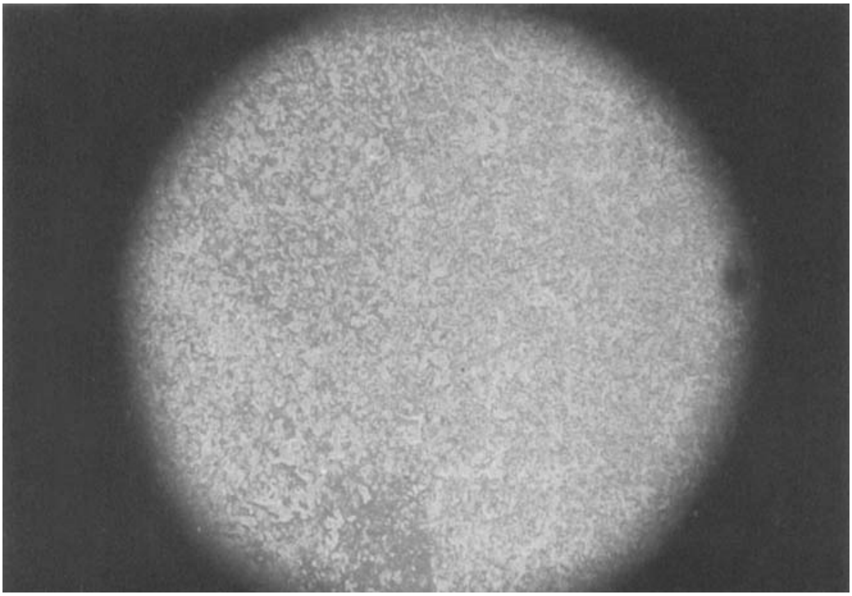

FIGURE 6 Microscopic picture of ROTN-101; before UV test. (Sample No. 7 in Table II).

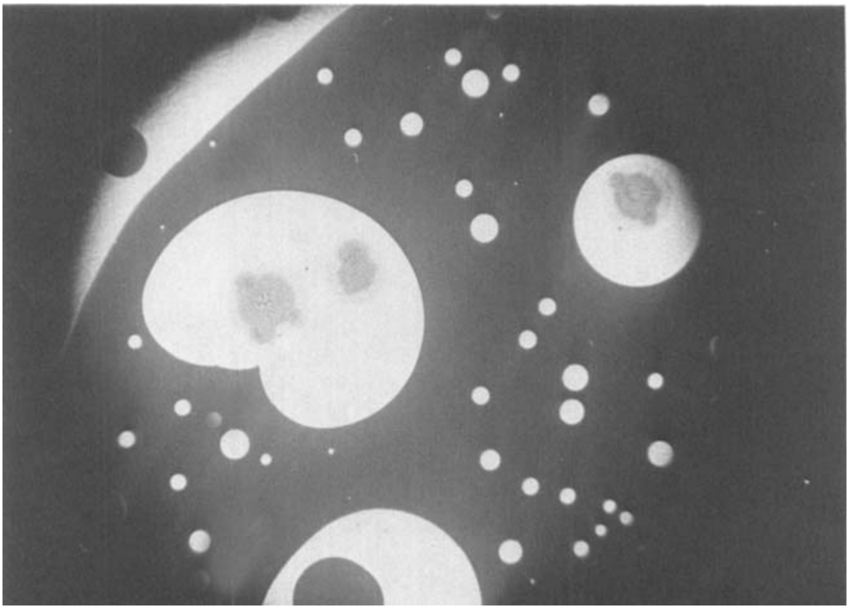

FIGURE 7 As Figure 6; after UV test. The dark area is the isotropic phase.

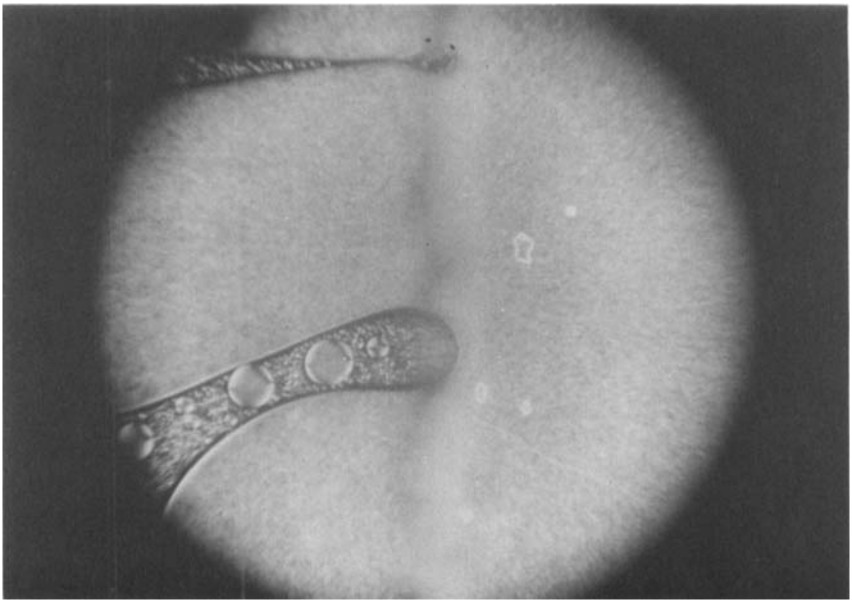

FIGURE 8 Microscopic picture of ROTN-101. (Sample No. 8 in Table II) The transition area after UV test. Left side: unexposed, right side: exposed to UV. Note the appearance of the isotropic phase (Dark areas).

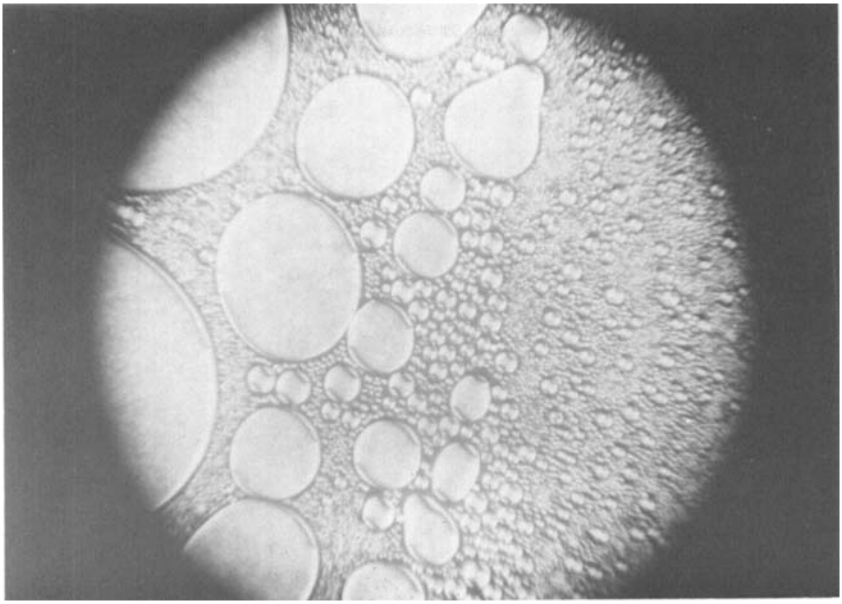

FIGURE 9 As Figure 8. The degraded area. Note that the "bubbles" are the remains of the original material.

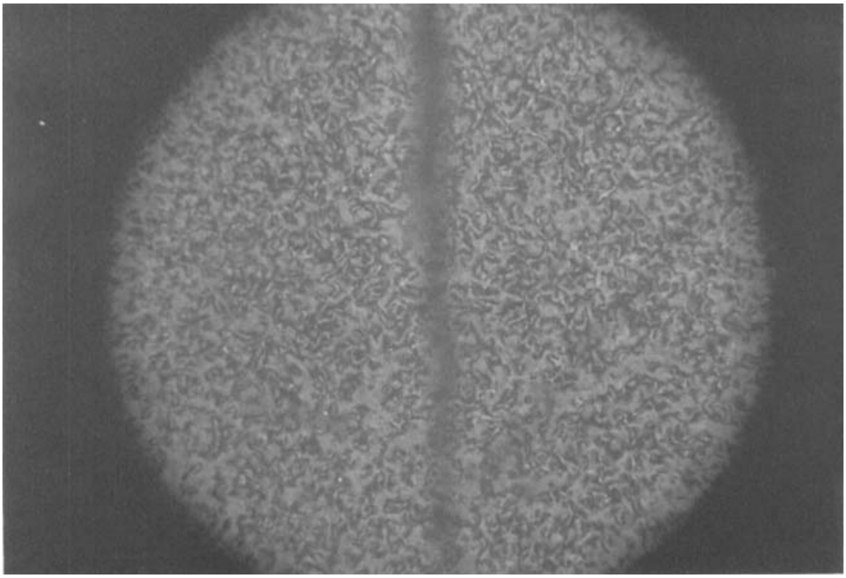

FIGURE 10 Microscopic picture of DIAMO in ROTN-101. (Sample No. 4 in Table II) Transition area. Left side: unexposed, right side: exposed to UV. No observable change in color.

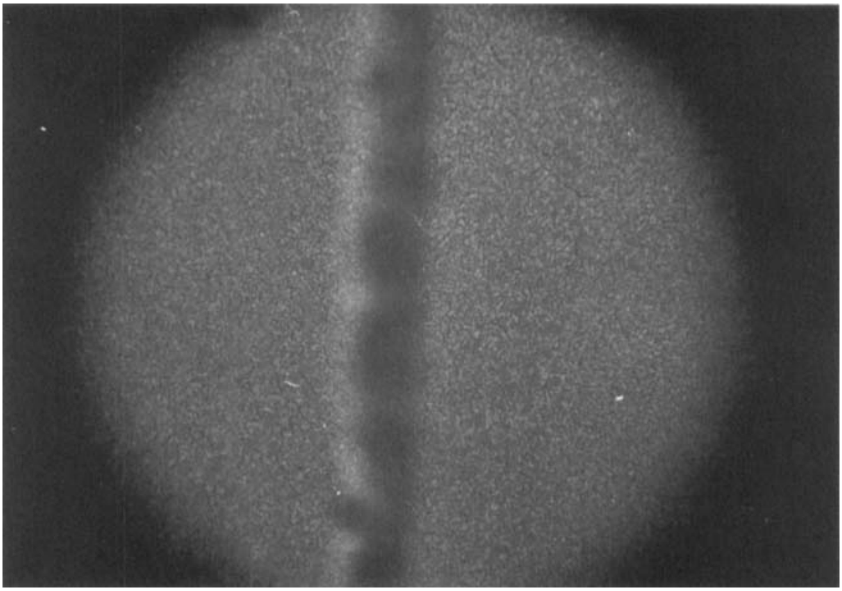

FIGURE 11 Microscopic picture of DIAMO in ROTN-101. (Sample No. 9 in Table II) Transition area. Left side: unexposed, right side: exposed to UV. No observable change in color.

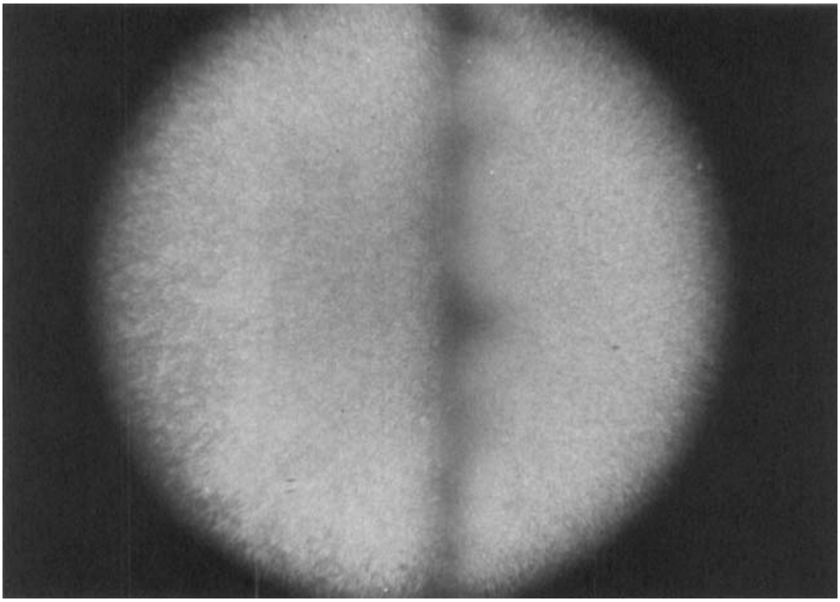

FIGURE 12 Microscopic picture of DIAMO + Sudan Black B. in ROTN-101. (Sample No. 5 in Table II) Transition area. Left side: unexposed, right side: exposed to UV. No observable change in color. (See also Figure 2 and Figure 11).

Now the main results obtained are summarized. The results of visual observations are in good agreement with the changes detected by the transmission spectra (TS). While by TS all differences throughout the whole spectrum can be demonstrated, by visual observation only differences near to the maximum of the relative visibility of colors are taken into consideration (fotopic adopted vision, V(λ) function).

In the course of our investigations two types of changes in the spectra were detected. Visually observed mixtures with no or minimum change in color showed parallel like shift of the TS; but the unstable mixtures showed different TS from the parallel ones. The fact that the change in the spectra is not a simple parallel shift, but considerable shifts in the maximum and minimum values of the wavelength were observed, predicts the dramatic change in color. A parallel shift of the original one would indicate a change in the state of orientation order only.

In the literature up to now little attention was paid to the stability problems. The applied categories of qualifying were "proper or improper", which are undefined expressions only. Therefore we try to discuss quantitatively and qualitatively this problem.

INTRODUCING THE UV STABILITY FACTOR (SF)

The TS in its original form should be an informative diagram showing the scale of changes in detail, but sometimes a single number or a "figure of merit on stability" would be more adequate for the quick quantitative comparison of dyes or mixtures with different UV stability.

Our measurements and observations confirmed, that such a factor can be applied for describing the measure of stability for UV light. The proposed stability factor (SF) on the basis of TS can be introduced as follows: The measure of change on the influence of UV exposure can be related to the change detected in the TS spectra. Let us consider the following expression:

$$B = \left| \int_{400}^{700} T_o(\lambda)\mathrm{d}\lambda - \int_{400}^{700} T_x(\lambda)\mathrm{d}\lambda \right| \qquad (1)$$

where

T_o (λ)—is the transmission as a function of wavelength before the UV test;

T_x (λ)—is the transmission as a function of wavelength after x hours of exposure.

B defined this way is a measure of the effective changes. It is suitable, if a high value of the stability factor should denote high stability and vice-versa. The inverse of B (1/B) satisfies this requirement.

Hence the proposed stability factor (SF) is:

$$SF_x = \left| \int_{400}^{700} T_o(\lambda)\mathrm{d}\lambda - \int_{400}^{700} T_x(\lambda)\mathrm{d}\lambda \right|^{-1} \tag{2}$$

The x index designates the hours of exposure.

Generally we do not perform the measurement at every λ. For the most part the approximation of the integrals by graphical integration meets the requirements. For example, by achieving a 10 nm resolution, the integrals can be replaced by the more convenient form:

$$SF_x = \sum_{i=1}^{n} \left| \Delta T_i \right|_x^{-1}; \tag{3}$$

where $|\Delta T_i|_x = |T_{io} - T_{ix}|$ and

T_{io}—is the transmission at i. th wavelength before UV test,

T_{ix}—is the transmission at i. th wavelength after x hours of exposure,

x—denotes the hours of exposure,

n—denotes the number of measuring points.

Thus, the SF_x stability factor allows quick comparison between different materials.

Making use of SF_x the classification according to the UV stability can be established. The abovementioned mixtures are listed anew in Table II, but now in the order of decreasing SF_x; that is, in order of decreasing stability. The results of the visual observations and the numbers of the relating microphotographs are also listed. The validity of SF_x can be checked by visual observation and by microscopic investigations.

The comparison among the quoted mixtures can be easily done by making use of the SF_x factor. According to Table II the most stable mixture is No. 1 with dye D 35 (highest SF_x). The second one is mixture No. 2 with dye D 16. (Independently from our results the BDH catalog gives the same order for stability on the basis of resistivity and of order parameter measurements.[6] Comparing E7 to ROTN-101 (Samples No. 3 and No. 7) by dividing simply the SF No. 3 with SF No. 7, a value of 2,5 is obtained. That means that the LC E7 is 2.5 times more stable than ROTN-101.

Let us compare now the SF values of the various dye + LC mixtures with the SF value of the respective host materials. In Table III these values are listed. These numbers indicate that in certain cases—at values greater than 1—the stability factor, that is the stability, is greater than that of the host material itself. This fact can be interpretated according to the following hypothesis: If a certain dye mixed to the LC host has high stability against UV light, it improves the stability of the whole system, and as a result the mixture shows higher UV light resistivity. On the other hand, if the dye possesses poor stabil-

TABLE II

Mixtures in the order of decreasing UV stability

No.	SF_x	Dye	Conc. in wt%	LC type	CB 15 in wt%	C 15 in wt%	Change by visual and microscopic observations	Number of microphoto	Hours of exposure
1.	2.61	D 35	1.62	E7	—	1	NO	—	56
2.	1.68	D 16	1.92	E7	—	1	NO	—	56
3.	0.95	—	—	E7	—	1	NO	—	56
4.	0.75	DIAMO	3.85	ROTN-101	—	—	NO	Figure 10	51
5.	0.57	DIAMO Sudan Black B.	3 2	ROTN-101	3	—	NO	Figure 12	52
6.	0.52	Forondunkelblau E-2RL Foronbrillantrot E-RLN	5.9 6.7	ROTN-101	1.35	—	SL	—	56
7.	0.38	—	—	ROTN-101	2.0	—	SL, I	Figures 6, 7	51
8.	0.35	—	—	ROTN-101	—	—	SL, I	Figures 8, 9	52
9.	0.27	DIAMO	3.85	ROTN-101	2.0	—	NO	Figure 11	51
10.	0.26	Foronrot E-2GL	8.3	ROTN-101	3.0	—	ST, I	Figures 4, 5	51
11.	0.23	Forondunkelblau E-2RL (fl)	6.5	ROTN-101	2.0	—	ST, I	—	56
12.	0.17	Foronbrillantrot E-2BL Forondunkelblau E-2RL	6.5 2.7	ROTN-101	—	—	VST, I	—	56
13.	0.15	Sudan Black B.	2.0	ROTN-101	3.0	—	VST, I	Figures 2, 3	51

NO —No change
SL —Slight change
ST —Strong change
I —Isotropic transition
VST—Very strong change

ity, that means, it is predisposed to ageing or to color changing, the stability of the mixture will be worse than that of the host material itself. On the base of this hypothesis a line can be drawn in Table III separating the numbers listed into two groups: > 1 and <1. The proposed relation for this concept (the *S*tabilizing *I*nfluence of *D*ye, SID) can be expressed:

$$\mathrm{SID}_{\mathrm{dye\text{-}LC}} = \frac{SF\,(\text{for dye} + \text{LC})}{SF\,(\text{for LC or LC} + \text{dopants})}\,.$$

Similarly by comparing two dyes:

$$\mathrm{SID}_{\mathrm{dye\text{-}dye}} = \frac{SF\,(\text{DYE No. } 1 + \text{LC})}{SF\,(\text{DYE No. } 2 + \text{LC})}\,.$$

Sample No. 13 in Table II is a dye containing azo-bonds. These types of dyes are known as very unstable ones. This fact is proved in our investigations as well ($SF = 0.156$ being the smallest value).

It was interesting that by adding a certain amount of stable DIAMO ($SF = 0.746$) to this sample, the mixture (Sample No. 5) showed a higher stability than the initial one ($SF = 0.156$). By comparing the two mixtures we get for SID the value 3.64. According to this fact it can conclude that certain dyes—for example DIAMO—exert considerable stabilizing influence even if the stability of the other dye in the mixture is very poor.

CONCLUSIONS

New dyes exhibiting liquid crystalline-like properties in the high temperature region were synthetized.

The longest member of these DTB derivatives (DIAMO) shows excellent solubility in various LC hosts. The dichroic ratio of DIAMO was measured and the value $A_R = 4.73$ was found. This is a medium value compared with those of other dyes but it indicates that DIAMO can be applied in dichroic LCDs as guest material.

This dye combines good solubility, relatively high positive dichroism and high UV stability, all these features render this material unique.

The UV stability tests revealed that mixtures of dyes having different chemical compositions show very different light resistance. Various forms of degradations were described and we proved that the stability of the LC host must also be taken into consideration. According to our results the exposure to strong light radiation can cause: change in color; change in the orientation (in the worst case this can lead to the appearance of isotropic phase).

We demonstrated that UV stability can be characterized by the figure of stability called STABILITY FACTOR (SF) and denoted by a single number. Making use of the classification according to the UV stability a rank of order

TABLE III

Stabilizing Influence of Dyes

Sample No. ··· Sample No. ···	1/3	2/3	4/8	5/7	6/7	7/8	9/7	10/7	11/7	12/8	13/7
SF for No. ··· SF for No. ···	2.74	1.76	2.12	1.49	1.37	1.08	0.71	0.70	0.60	0.49	0.41
Stabilizing Influence of Dye SID	More stable than without dye SID > 1						SID < 1 No stabilizing effect				

can be established for a series of dyes, LC hosts and mixtures as well. Our experiences indicates that in the case of strong UV illumination an acceptable level of stability is SF $\geqslant 0.5$.

On the basis of our hypothesis a new concept, the STABILIZING INFLUENCE of DYE (SID) was introduced, by which we can express the influence of various dyes for LC host, and which gives the measure of stability of one dye compared with others.

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