

Development of Color Resists Containing Novel Dyes for Liquid Crystal Displays

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In recent years, the use of liquid crystal displays (LCD) has shown a great expansion into devices such as Smartphones and tablet PCs in addition to TVs and computer monitors. However, LCDs have issues such as low aperture ratio as a consequence of their high-definition and insufficient battery capacity. Improving the brightness of the color filter is expected to become one of the solutions for these issues. We have launched the DyBright® series of color photoresists which contains novel dyes, and which can contribute to improving the brightness of color filters. This report introduces the development of these novel dyes for color photoresists.

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Introduction

In addition to conventional uses in televisions, monitors, notebook computers and mobile phones, liquid crystal displays (called LCDs in the following) have been further integrated into our daily lives in devices such as smart phones, tablet computers, game machines and music players. They have developed to the extent that almost no day goes by in which we do not see an LCD. The technical issues for LCDs, which have developed in this manner, are as follows. These issues include increases in power consumption accompanying increases in screen size, reduction in the aperture ratio of color filters with higher definition devices and battery insufficiency in devices used portably. One solution for these problems is improving the brightness of color filters, which are constituent components of LCDs.^{1), 2)}

At present, the main current in color filters is their consisting of primary color pixels of red, green and blue, and with LCDs, images and video are displayed by controlling and switching the amount of light passing

through each color filter for each pixel instantaneously by a liquid crystal shutter. Improving the brightness of color filters comes down to improving the brightness of each pixel,³⁾ in other words, improving the transmittance of color resists, which are the materials that form the pixels.

In addition to resist components, color resists have colorants mixed in, and color performance is mainly determined by the colorants. Currently, color resists for LCDs use pigment dispersed resists in which pigments are sub-micro-dispersed for the colorants. In the early days of color filters, there were color filters manufactured by dyeing casein with dyes,⁴⁾ and pigment dispersed resists in which pigments were used as colorants were not used from the standpoint of productivity, color density and durability.

Here we will discuss pigments and dyes, which are the focal point of this article. Pigments and dyes are used for forming color coated films and dyeing fibers respectively, and both of them are colorants; however, they are classified according to whether they are insoluble in solvents and are in a dispersed state or whether

Table 1 Properties of conventional pigments and dyes for color resists

Colorants	Physical properties of colorants				Properties of resist film		
	Form at use	Unit	Size of unit	Interfacial area/molecule in unit	Heat resistance	Light fastness	Solvent resistance
pigments	insoluble	particle	around 50nm	small	good	good	good
dyes	soluble	molecule	< 10 nm	large	poor	poor	poor

they are soluble and in a dissolved state when used. (There are some dispersed dyes that are used in a dispersed state for dyeing polyester fibers, but in such cases, classification in terms of application for the material used for dyeing, that is the dye, is recognized.) **Table 1** summarizes the physical properties of colorants when used specifically in color resists and the general features of the resist films that are formed.

Limitations of Pigment Dispersed Resists and Possibilities for Dyes

The type of pigment used in a color filter is selected because of the suitability of the brightness and micro-dispersion stability. There has been a gradual improvement in performance, and the types of pigments that can be used have become fixed. Improvement in the brightness of pigment dispersed resists has peaked, and their insufficient contrast caused by light scattering due to the pigment particles has been pointed out.

LCDs have a structure in which a color filter and liquid crystal layer are sandwiched between two polarizers. The design is such that light output by a backlight has only the light oscillating in a certain direction extracted when it passes through the first of the polarizers, and the amount of light passing through the second polarizer is controlled next by controlling the direction of the vibration with the liquid crystal layer. However, in current color filters, the pigment particles scatter light; therefore, scattered light other than the incident light arises. In this instance, light leaks arise because of light scattering even in a dark display state, and picture quality is affected adversely.⁵⁾ The value for the brightness during bright display divided by the brightness during dark display is treated as the contrast, and this is as important as brightness for the color performance of a color filter.⁶⁾

Various molecular structures for dyes have been made practical, and among them, ones having sharp hues that come through with high brightness are known. In addition, unlike pigments, it is possible for them to be present within a film as molecules; therefore, there is no light scattering effect, and ultimately, achievement of high contrast can be expected.⁶⁾

Around the year 2000, the situation was one in which LCDs still needed much improvement in terms of brightness and contrast, and pigment dispersed resists had reached a peak in terms of color performance, so various companies investigated the use of dyes. However,

because of problems with elution of dyes in the manufacturing processes for color filters and insufficient heat resistance or insufficient light resistance caused by dyes, we did not see any coming into practical use. Thereafter, investigations into the application of dyes were generally not carried out for several years.

However, since Sumitomo Chemical has been a dye maker for a long time, it aimed at a dramatic improvement in the performance of color filters by applying its dye technology to color resists and started afresh on verifying the possibilities for dyes. Not only were screening investigations for a large number of dyes carried out, but also, as a result of investigations into resist compositions for optimizing matching between the dyes and other components and carrying out matching of compositions that could withstand use in color filter manufacturing processes, we had the industry's first success in developing and marketing the DyBright® series, which is a series of color resists with improved brightness, improved reliability and other properties that can withstand use in color filter manufacturing processes. In this article, we will give a simple introduction to the development of these dyes.

Spectrum and Brightness

The transmittance spectra of red, green and blue pixels created using pigment dispersed resists are shown in **Fig. 1**. Improvements in transmittance at the transmission maximum for each of them are necessary for improving brightness. Even though the transmittance at the transmission maximum can be increased if the pigment content in the pixel is simply reduced when the film thickness is made constant, the overall transmittance is increased, and the coloration requirements of customers cannot be satisfied. To satisfy the film

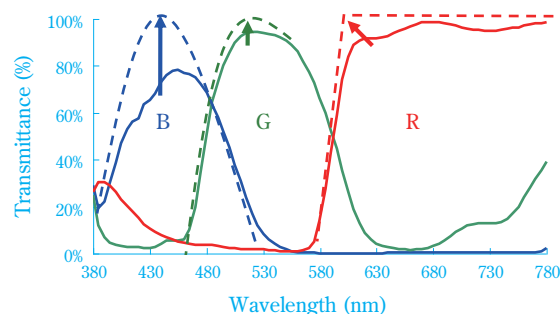


Fig. 1 Transmittance spectra of Red, Green and Blue—experimental spectra (solid line) and target spectra (dot line)

thickness and coloration required by customers and to improve the brightness, a square spectrum, with a spectral shape in which the wavelengths that should be absorbed are absorbed and only the wavelengths that should be transmitted are transmitted to the extent possible, is ideal. However, there are no colorants that exhibit a square spectrum, and realistically, those shown by the dashed lines in **Fig. 1**, for example, can be thought of as a target model.

Among red, green and blue, the transmittance peak for blue pixels is relatively low, and since it is also desirable to improve blue to improve the brightness as a whole while maintaining balance during white display, we gave this priority when carrying out our investigations. The pigments used in the blue pixels in **Fig. 1** are a combination of C. I. Pigment Blue 15:6 and C. I. Pigment Violet 23 (**Fig. 2**). In the investigation, there was a need for coloration with a transmittance in a coating film state higher than these pigments⁷⁾ that are normally used. In addition, LED light sources have become the main current in LCD backlights, and these light sources have a strong light emission peak in the neighborhood of 445 nm. The greater the overlapping region in the transmission spectra of this spectrum and the pixel, the greater the amount of light transmitted becomes, making for an improvement in brightness (type **Fig. 3**). As a first step in improving the transmittance of blue pixels, we began our improvements by improving the transmission spectrum of the violet coloration used as a complementary coloration for color adjustment.

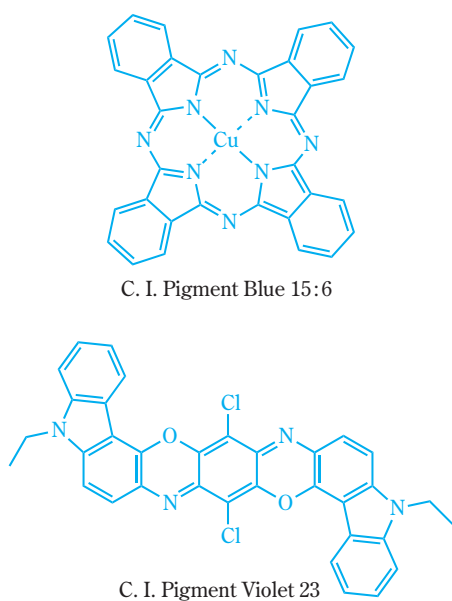


Fig. 2 Structure of C. I. Pigment Blue15:6 and C. I. Pigment Violet 23

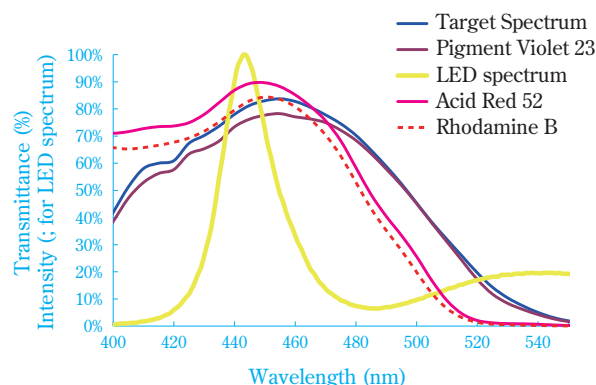


Fig. 3 Target spectrum, LED spectrum and transmittance spectra of several dyes

Development of 1st Blue (Violet Colorant for First Generation Blue Resist)

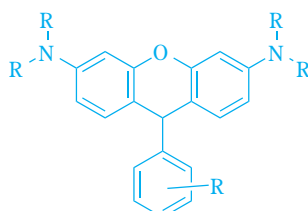
As a substitute for C. I. Pigment Violet 23, we investigated a dye having high transmittance in the 450–500 nm region. From the Sumitomo Chemical database of the many dye structures and their various physical properties, which we have built up as a dye maker, we searched for chromophores suitable for a violet dye, and came up with xanthene, cyanine, azo, anthraquinone, dioxazine and triphenylmethane structures as candidates. A comparison of the basic performance of the six chromophores is given in **Table 2**.

We narrowed the six dye groups down to cyanine and xanthene, which had the highest possibilities for high transmittance and carried out initial performance evaluations using commercial products or samples which we had primarily synthesized. The light resistance of both dye groups alone was poor, but with mixed usage conditions of C. I. Pigment Blue 15:6 for the xanthene, suitability for this use was confirmed, inclusive of heat resistance and light resistance. Thus, we decided to pursue dye development centered on a xanthene system first.

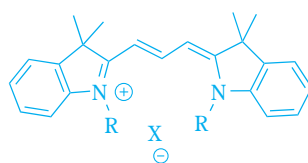
Rhodamine B is known as a typical commercial product for xanthene (**Fig. 4**). Rhodamine B has a maximum peak for transmission at 455 nm and exhibits comparatively high transmittance in this neighborhood, making it a compound with a desirable spectrum. However, since the absorption at 460–500 nm is stronger than the target spectrum, the amount of light transmitted in this region is low, and improvements in brightness cannot be expected. The goal is improving transmittance in the neighborhood of 450 nm and having a spectrum identical to C. I. Pigment Violet 23 in the 460–500 nm region,

Table 2 Properties of dyes (⊙: Good, ○: Moderate, △: Poor) and dye structures

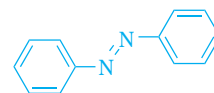
	Xanthene	Cyanine	Azo	Anthraquinone	dioxazine	Triphenylmethane
Potential of high transmittance	⊙	⊙	△	△	○	○
Heat resistance	○	△	○	○	○	△
Light resistance	△	△	○	○	○	△
Easiness of synthesis	○	○	⊙	△	△	△



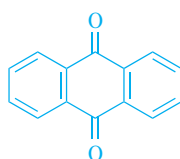
Xanthene



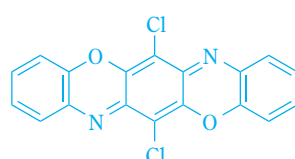
Cyanine



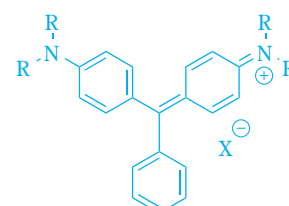
Azo



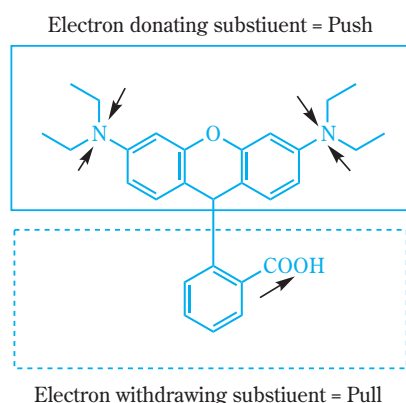
Anthraquinone



dioxazine



Triphenylmethane

**Fig. 4** Structure of Rhodamine B

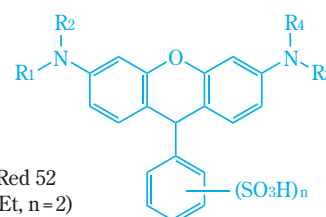
and therefore, increasing the wavelengths of the transmission spectrum for Rhodamine B was necessary.

Techniques for increasing transmission spectrum wavelengths

Rhodamine B expresses red ($\lambda_{\text{max}} = 555 \text{ nm}$) in an organic solvent. Xanthene systems, starting with Rhodamine B, take the form of push-pull color parent structures through control of the electron state by substituents. In other words, they have structures formed from partial structures (solid lines) that are electron donors within the molecule and partial structures (dashed lines) that are electron acceptors (**Fig. 4**).

Typically, to increase the wavelengths for the color transmission spectrum, the effect of the electron donor part must be strengthened, and at the same time, the

effect of the electron absorbing part must also be strengthened. C. I. Acid Red 52 has this concept and is a xanthene dye having more absorbency on the long wavelength side than Rhodamine B. It can be acquired easily as a commercial dye. C. I. Acid Red 52 is a compound in which the electron absorption has been strengthened and has the same structure as Rhodamine B for the electron donor part, with two sulfonic acid groups added to the structure of the electron absorbing part (**Fig. 5**). The solution absorption spectrum has expanded absorption of 10 nm on the long wavelength side compared with Rhodamine B, and the transmission spectrum also has increased wavelengths in the 460–500 nm region. However, the absorption in the 460–500 nm region is still strong, and the targeted transmission spectrum was not obtained. In addition, when C. I. Acid Red 52 was actually evaluated in a resist, the light resistance was extremely poor; furthermore, water solubility was high due to the effects of its having two sulfonic acid groups, and there was a problem in that

C.I. Acid Red 52
($R_1 \sim R_4 = \text{Et}$, $n = 2$)**Fig. 5** Structure of examined Xanthene dyes

dissolution in the organic solvents used for resists was insufficient.

Compounds having xanthene skeletons are attractive in terms of transmission spectrum, but there are few types found as commercial dyes, and we could not find one that could be used in this application. Therefore, we decided to develop a new xanthene compound. Development of Sumitomo Chemical's own xanthene dye progressed with C. I. Acid Red 52 as the lead compound. Since C. I. Acid Red 52 could not be dissolved in a resist solution because of its excessive solubility in water, the sulfonic acid groups were reduced to one. As a result, there was a reduction in the electron absorption capacity in the structure for the electron absorbing part, resulting in a shift to shorter wavelengths than C. I. Acid Red 52. Thus, substituent R_D, with greater electron donor properties than substituents R₁ and R₃ was introduced to strengthen the electron donor properties of the structure for the electron donor part. With the introduction of this R_D, the transmittance in the neighborhood of 450 nm improved and a transmission spectrum equal to or greater than C. I. Pigment Violet 23 could be obtained in the 460–500 nm region.

Next, we carried out a variety of substitution screenings for different types of substituents in the same manner for R₂ and R₄ and decided on R₂ and R₄ after making comprehensive judgments based on ease of synthesis,

yield and manufacturing costs. We confirmed that the spectrum was more favorable and that the brightness was improved, but the solubility in resist solvents was insufficient. Therefore, one more reaction step was added for the R_D substituent, and we were successful in giving high solubility by chemical functionalization and obtained the new xanthene dye 1st Blue. The transmission spectrum for the new xanthene dye 1st Blue is shown in Fig. 6. It was possible to achieve transmittance higher than C. I. Pigment Violet 23, which is a pigment.

Table 3 gives a comparison of the performance of a pigment blue resist and a first generation DyBright® Blue resist. The brightness of the blue pixels was improved 6%, and performance with an equal or greater reliability was obtained. There was a fear of lowering the heat resistance and light resistance by changing the colorant from a pigment to a dye, but by introducing a sulfonic acid group to the substituents, hydrogen bonds operated, and the stacking effect between molecules became stronger, so excellent heat resistance was obtained. In addition, the reduction in light resistance was slight because a good balance was maintained in the electron distribution between the structure for the electron absorbing part and the structure for the electron donor part. Thus, Sumitomo Chemical completed the development of 1st Blue as the first generation dye for the DyBright® series.

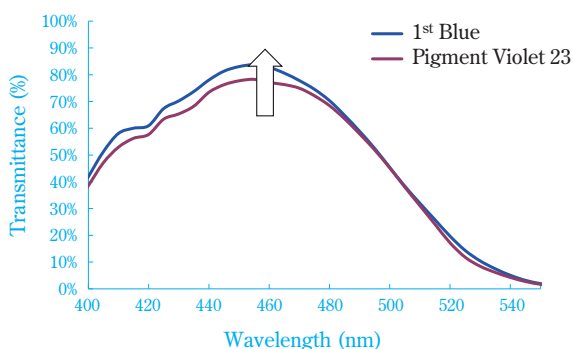


Fig. 6 Transmittance spectrum of novel Xanthene dye 1st Blue

Development of 2nd Blue (Violet Colorant for Second Generation Blue Resist)

With 1st Blue, brightness that could not be achieved with existing pigments was achieved for a first generation violet colorant, but transmittance was still relatively low compared with the red and green pixels, and there was margin for further improvement. We moved on to the development of a second generation violet colorant, aiming at further improvements in transmittance. Since a great deal of knowledge was obtained about xanthene systems in the process of finding the first generation

Table 3 Properties of pigment resist and DyBright® (Each durability test result shows ΔE_{ab}^* that is color change before and after tests)

resists	Brightness	Heat resistance (230°C, 2hrs)	Light fastness (Xe lamp, 48hrs)	Solvent resistance (dipping in NMP)
Pigment (B15:6/V23)	100%	5.0	1.6	0.3
1st Gen. DyBright® Blue	106%	2.0	1.9	0.2
2nd Gen. DyBright® Blue	110%	3.0	2.9	0.1

xanthene dye 1st Blue, we also planned on using that knowledge in the second generation, and proceeded to continue our investigations of xanthene systems. The goal was (1) to have transmittance higher than the first generation 1st Blue and (2) to obtain a transmission curve having a transmission region the same or greater than 1st Blue in the 460–500 nm region.

Of these, goal (2) meant controlling the shape rather than lateral movement of the spectrum was a difficult problem to achieve with the investigations along the line of extension up to this point. We reassessed the details of the types and combinations of substituents on N in Fig. 5, and during the investigation, we found that, particularly in the combination of substituents, the peak width at half height of the absorption spectrum narrowed and a steep shape was exhibited. In other words, this was synonymous with the spectrum changing in a direction that satisfied the item in (2) for the transmission spectrum (Fig. 7). Furthermore, the narrowing of the peak width at half height improved the color concentration of the dye and, along with this increase, the contrast between the absorption peak in the neighborhood of 550 nm and the transmission peak in the neighborhood of 450 nm; therefore, color design that improved the transmittance for the transmission peak for the constant absorption necessary for achieving a constant coloration became possible, and development of 2nd Blue that satisfied goals (1) and (2) was completed.

In the first generation investigations, the solution was found mainly by verification of the effects of substituents on electrons, but with the second generation, it can be said that we were successful in finding an even higher level solution by understanding the new factor of controlling the steric repulsion between substituents themselves and the rotational movement of the molecule in addition to this.

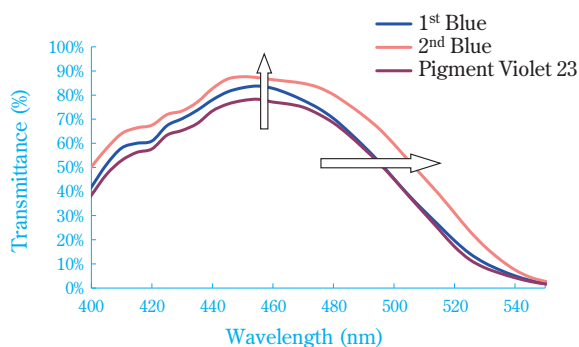


Fig. 7 Transmittance spectrum of novel Xanthene dye 2nd Blue

Conclusion

We are currently continuing investigations into the development of a third generation of new dyes to develop blue pixels having even greater brightness. In addition, we are developing new dyes to achieve improvements in the brightness of not only blue, but also red and green.

In this article, we have mainly discussed molecule design techniques for improving brightness, but for making the practical use of dyes possible, not only brightness, but also heat resistance, light resistance, dye solubility in solvents and many other hurdles for practical use must be cleared, and development for these is not at all easy. Moving forward, we will continue our efforts, and by developing the next generation of the DyBright® series, we hope to be able to continue to provide solutions for various LCD problems, such as increasing the brightness of color filters.

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