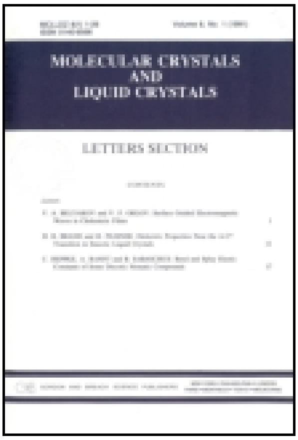

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Synthesis and Characterization of Modified Dyes for Dye-Based LCD Color Filters

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Color filters (CFs) are important elements for making color images in liquid crystal displays (LCDs) and other imaging devices. A colored layer is fabricated with colorants of red, green, and blue from either dyes or pigments. These colorants are arranged uniformly and make up the CF while also converting white backlight into a color image. The pigment is advanced to thermal stability, light resistance and chemical resistance, so many used for manufacturing color filters. However, the color filters manufactured with pigments have spectral drawbacks such as decreased transmittance of light and decreased contrast ratio both caused by aggregation of pigment particles. Thus, it is necessary to do the expensive and time-consuming dispersion process for obtaining stable and finer pigment millbases without molecular aggregation.

In this study, our focus was on a new series of acid dye systems that have alkyl amine groups because it has an advantage in solubility of organic solvents.

As a result of our focus, we have designed and synthesized new acid dyes that consist of alkyl amine groups, using a simple method of reaction. In addition, manufacturing color filters without the milling process in the optical characteristics, thermal, chemical stability were investigated.

Keywords Acid dyes; alkyl amine; aminated dyes; LCD color filter

Introduction

Color filters (CFs) are important elements for making color images in liquid crystal displays (LCDs) and other imaging devices. In general, a color filter consists of a clear substrate, a black matrix, a colored layer, a overcoat layer and an ITO film. The colored layer is fabricated with colorants of red, green, blue from either dyes or pigments. These colorants are arranged uniformly to make up a CF, and convert white backlight into a color image [1–2].

In manufacturing a CF, there are four traditional processes used: dyeing, pigment dispersion, printing, and electro-deposition [3–7]. Among these, the pigment dispersion method has been widely used in the mass production of CF for LCD since it can produce a CF of good color reproducibility and a high resistance to heat, light and chemicals. However, this method has spectral drawbacks such as a decreased transmittance of light and a contrast ratio caused by aggregation of pigment particles. Due to these drawbacks,

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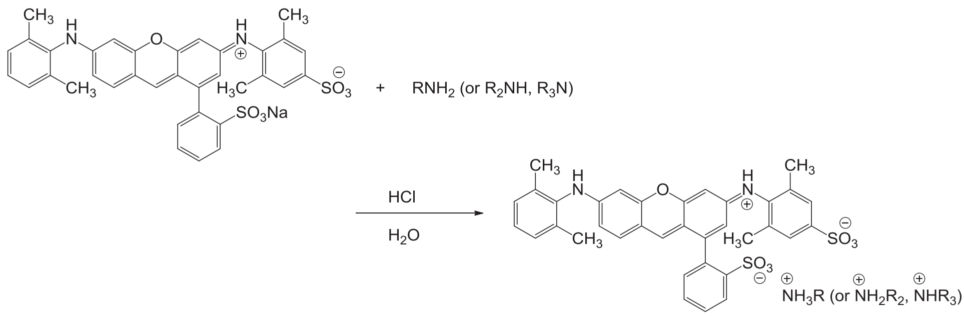
doing the expensive and time-consuming dispersion process for obtaining stable and finer pigment millbases without molecular aggregation was necessary [8–9].



Scheme 1. Synthetic route.

On the other hand, since dyes can be dissolved in a media and exist in molecular phase and have less light scattering, dye-based CF can have higher transmittances and contrast ratios. Manufacturing dye-based CF does not require a dispersion process due to their excellent solubility in organic solvents. However, previous studies have shown that thermal, light and chemical resistances of dye-based CF are limited only to commercial production and application of LCD color filters [3].

In this study, our efforts have focused on a new series of acid dye systems that have alkyl amine groups because they have advantages in solubility of organic solvents.

Thus, we have designed and synthesized new acid dyes that consist of alkyl amine groups through a simple method of reaction. In addition, manufacturing CF without using the milling process in the optical characteristics, thermal and chemical stability was investigated.

Experimental

Synthesis

C.I. Acid Red 289 (1eq) was stirred with distilled water (20ml) at room temperature. After the dye was completely dissolved, a mixture of alkyl amine (1eq, if the dyes had two sulfonate groups, using 2eq of alkyl amines) and hydrochloric acid aqueous solution (1.1eq, if the dyes had two sulfonate groups, using 2.2eq of HCl) was added slowly dropwise. After

Table 1. Yield of aminated dyes

Sample	Alkylamine	Yield (%)
1	Dodecyl	86.5
2	Hexadecyl	79.0
3	Dibutyl	49.2
4	Dihexyl	81.1
5	Dioctyl	73.9
6	Dimethyl-n-octyl	71.7

Table 2. Components of synthetic dye-based color resist ink

	Contents(g)
Synthetic dye	0.1
Binder	2.0
Solvent	
PGMEA	1.7
Methanol	1.7
Photo resist[a]	4.5
Total	10

[a]Total of solid content (%) of 24.0% acrylic photo resist.

the dropping, the mixture was stirred for 3 hours at room temperature. When the reaction was complete, the reactant was heated to over 60°C. Then, the mixture was directly filtered off and washed with hot water several times. Finally, the cake was washed with a 30% methanol aqueous solution. The red powder product was dried under vacuum at 60°C. The alkyl amines which were used in this study were as follows: dodecylamine, hexadecylamine, dibutylamine and dihexylamine (Scheme 1). Table 1 shows each of the aminated dyes that were yielded.

Fabrication of an aminated dye-based color filter

Color resist ink composed of 1.8% millbase of each of the synthetic aminated acid dyes, 24% acrylic photo resist, propylene glycol mono methyl ether acetate (PGMEA) and methanol as solvent (Table 2). The mixture was magnetically stirred at room temperature for at least 30 minutes in a dark room without going through the milling process. After stirring, the mixture was kept from being exposed to light. For high adhesive strengths of colored film on the glass substrate, a spin coating of hexamethyldisilazane (HMDS) was done under the condition of 1000 rpm for 5 seconds and then 3500 rpm for 25 seconds. Post baking after the spin coating of HMDS was performed in an oven at 100°C for 90 seconds [10]. The resulting color resist ink was coated on transparent glass substrates that had been treated by HMDS. This treatment used a WS-400B-6NPP-LITE spin coater. Then a small glass sheet (5 cm × 5 cm) was coated with the prepared color resist, and was coated at a speed of 300 rpm for 15 seconds. After color resist coating, the coated color filters were placed upright on a flat table at room temperature for 3 minutes. Next, the coated color filters were soft baked

Table 3. Components of the synthetic dye millbase

Aminated dye millbase	Contents(g)
Aminated dye	1.2
Binder	1.1
Solvent	
PGMEA	3.7
Methanol	4.0
Total	10

Table 4. Components of the millbase mixture color resist

Reference millbase (PB15:6)		Aminated dye millbase	
100%	5.50g	0%	0g
95%	5.23*g*	5%	0.27*g*
90%	4.95*g*	10%	0.55*g*
85%	4.68*g*	15%	0.82*g*
80%	4.40*g*	20%	1.10*g*
75%	4.13*g*	25%	1.37*g*
		Contents(g)	
Millbase mixture		5.5	
Photo resist[a]		4.5	
Total		10	

[a]Total of solid content (%) of 24.0% acrylic photo resist.

in an oven at 80°C for 10 minutes to evaporate the solvent from the filters. After that, the coated layers were exposed to a high mercury lamp (300 W of strength at 365 nm) for 40 seconds. Finally, the color filters were hard baked at 230°C for 20 minutes to cure the glass substrate.

Fabrication of the mixture of blue pigment and aminated dye-based color filter

Color resist ink was composed of 12% millbase of reference blue pigment (pigment blue 15:6, Fastogen blue EP-CFX), 12% millbase of aminated red 289 dye, 24% acrylic photo resist, methanol and PGMEA which was used as a solvent. Tables 3 and 4 show the components of the millbase mixtures and color resist inks. The mixtures were stirred at room temperature for 30 minutes in a dark room without going through the milling process. After stirring, the mixture was kept from being exposed to light. Glass substrates were subjected to a pretreatment spin coating of HMDS at 1000 rpm for 5 seconds and then 3500 rpm for 25 seconds. Post baking after this spin coating was performed in an oven at 100°C for 90 seconds [10].

Pretreated glass sheets were coated with this prepared color resist by a spin coater at a coating speed of 300 rpm for 15 seconds. After the coating, the coated color filters were placed upright on a flat table at room temperature for 3 minutes. Next, the coated color filters were soft baked in an oven at 80°C for 10 minutes to evaporate the solvent. After that, the coated layers were exposed using a high mercury lamp (300 W of strength at 365 nm) for 40 seconds. Finally, the color filters were hard baked at 230°C for 20 minutes to cure the glass substrate.

Investigation of thermal stability

The dyes and coated colored films were screened for thermal stability by TGA and UV-visible spectrophotometer. In the TGA test, a sample was heated to 500°C to determine its degradation temperature and the conditions were set to a heating rate of 10°C/min under nitrogen atmosphere. A sample of the neat dyes film was heated to 80°C and held at 80°C for 10 minutes to remove an residual water or solvent. It was then heated to 230°C and held there for 20 minutes to simulate the CF manufacturing processing thermal conditions. The measured transmittance of the colored films showed thermal stability as differences 80°C and 230°C.

Investigation of chemical stability

During the LCD fabrication process, the CF are exposed to generally used solvents. It was found that chemical stability is a significant factor in the fabrication of CFs. The colored films were dipped into strong polar solvents such as *N*-methyl-2-pyrrolidone (NMP), propylene glycol mono methyl ether acetate (PGMEA) for 30 minutes. Before and after this chemical treatment, the chemical stability was evaluated by the CF chromatic changes.

Investigation of color purity improvement

Prepared color resists consisting of mixtures of reference blue pigment and synthetic dye millbase were coated to different ratios of millbase. A test for color purity improvement was conducted in which the color resist samples were made up of increasing 5 wt% synthetic dye against reference blue pigment 15:6 millbase. The UV-visible transmittance spectrums of each of the films were measured and investigated color coordinate to change of the reference blue color. In addition, when the colored film had a high ratio of synthetic dye millbase, it was found to affect in thermal resistance.

Results and Discussion

The structure of the dimethyl-n-octylaminated acid red 289 dye which was expected to be the most stable, was analyzed. Figure 1 displays the ^{1}H-NMR spectra of dimethyl-n-octylaminated acid red 289 dye. It was compared between the spectrum of acid red 289 dye and aminated acid red 289 dye. As the reaction proceeded, the alkyl amine group was created. In Fig. 1, ^{1}H-NMR spectra showed six different peaks at 9.12 ppm, 3.00 ppm, 2.74 ppm, 1.57 ppm, 1.26 ppm and 0.86 ppm indicating the each of peaks NH, *N*-CH_3, *N*-CH_2, vinyl CH_2, and CH_3, respectively.

Color filters should have high heat resistance during the formation of the alignment layer. The thermal stability of the dyes was investigated through observing their changes in transmittance spectra by baking the film at 80°C for 10 minutes and 230°C for 20 minutes (Fig. 2). In Fig. 3, thermal stability of the dye is investigated through measuring their changes in weight at more than 230°C, by TGA analysis. Dimethyl-n-octylaminated acid red 289 dye exhibited below 3% weight loss at 230°C.

Table 5. Chemical resistance test of synthetic dye-based color filter : chromatic change (ΔE_{ab}) after dipping for 30 min

	Chromatic change(ΔE_{ab})					
Chemical	Dodecyl (1)	Hexadecyl (2)	Dibutyl (3)	Dihexyl (4)	Dioctyl (5)	Dimetyl-n-octyl (6)
PGMEA	1.67	1.46	0.92	0.22	0.81	1.10
NMP	1.37	1.27	0.63	1.33	1.83	0.81

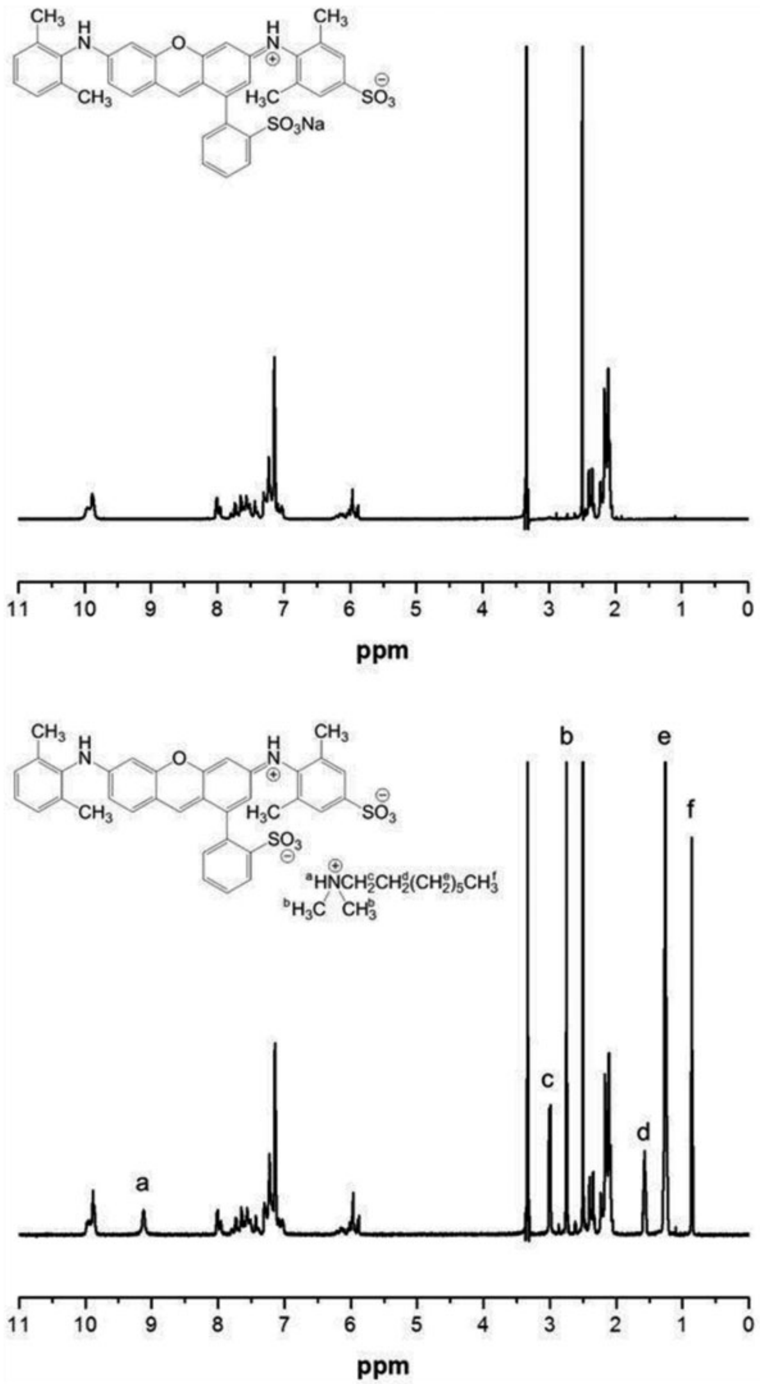


Figure 1. [1]H-NMR spectra of acid red 289 dye and dimethyl-n-octylamina-ted acid red 289 dye.

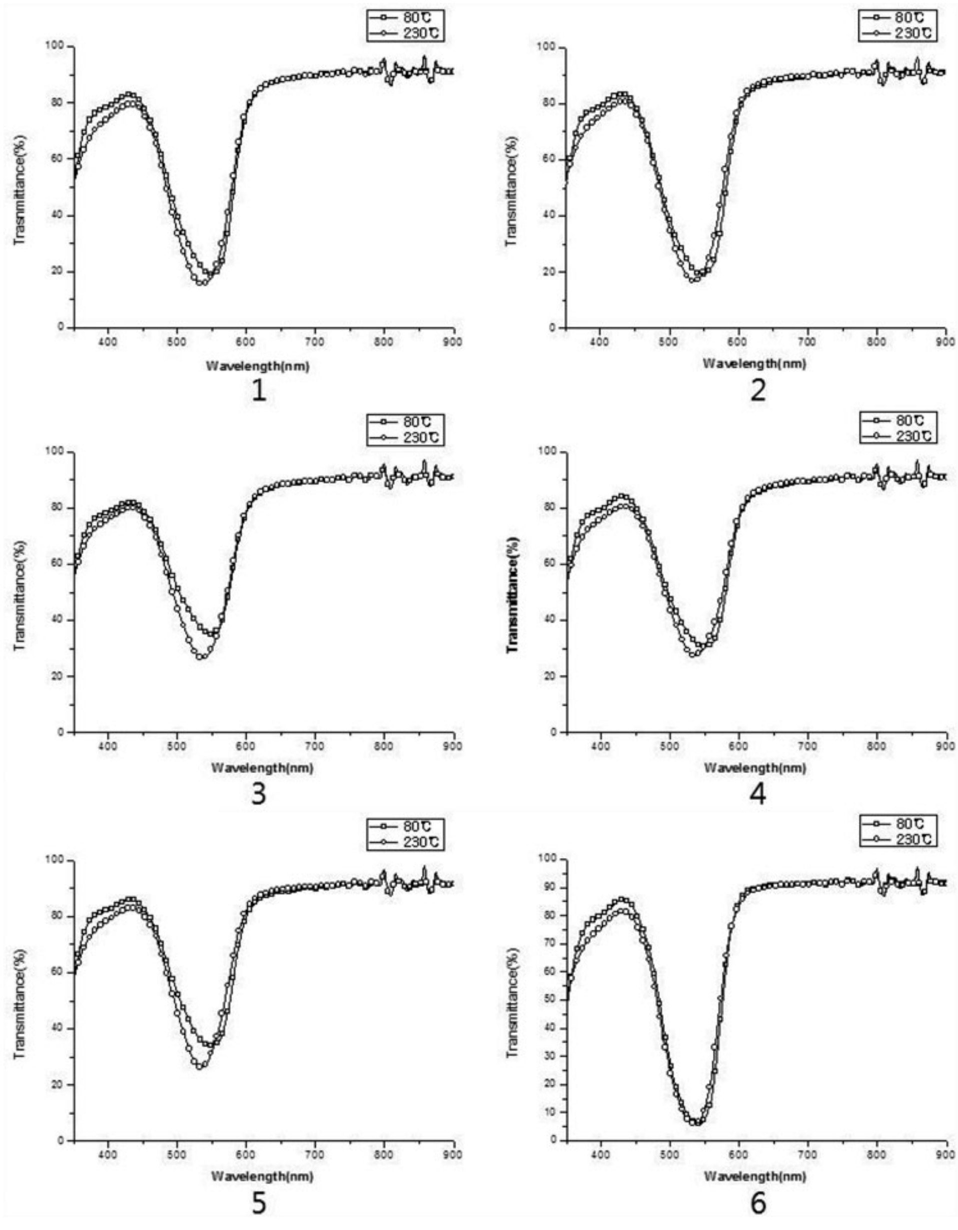


Figure 2. UV-visible transmittance for the thermal stability of films (1–4) at 80°C and 230°C.

In the thermal stability test, data show that the aminated acid red 289 dyes have good heat resistance. The chemical stability was investigated by both surface statement observation and chromatic changes. After dipping the synthetic dye-based color resist coated films into the above mentioned chemical solutions for 30 minutes at room temperature, CF surfaces were found to be stable; neither swelling nor peeling was observed. The chromatic change (ΔE_{ab}) was less than 3, indicating very good chemical stability (Fig.4; Table 5).

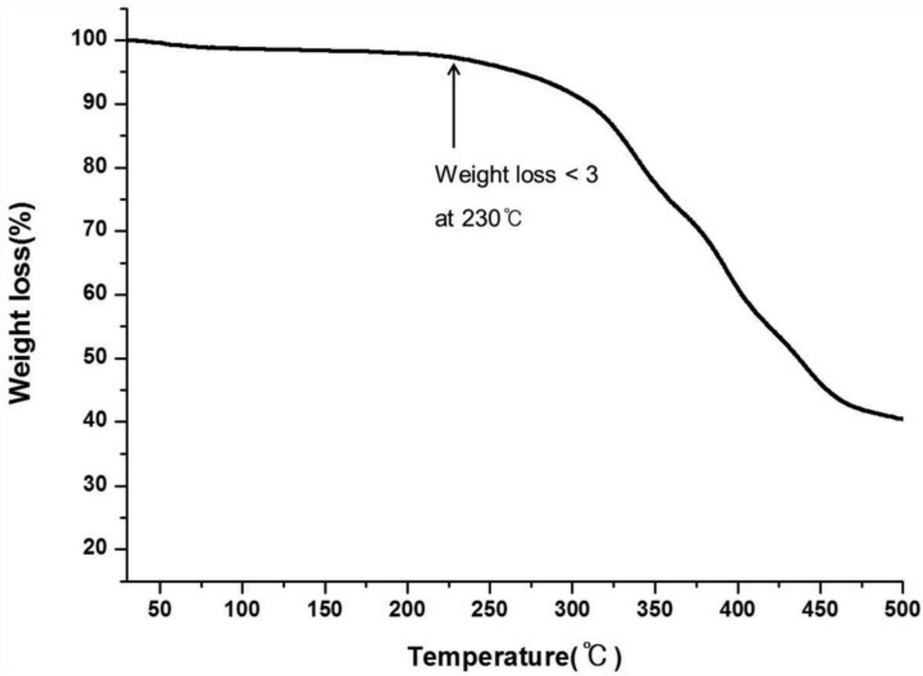


Figure 3. TGA curve of dimethyl-n-octylaminated acid red 289 dye (6).

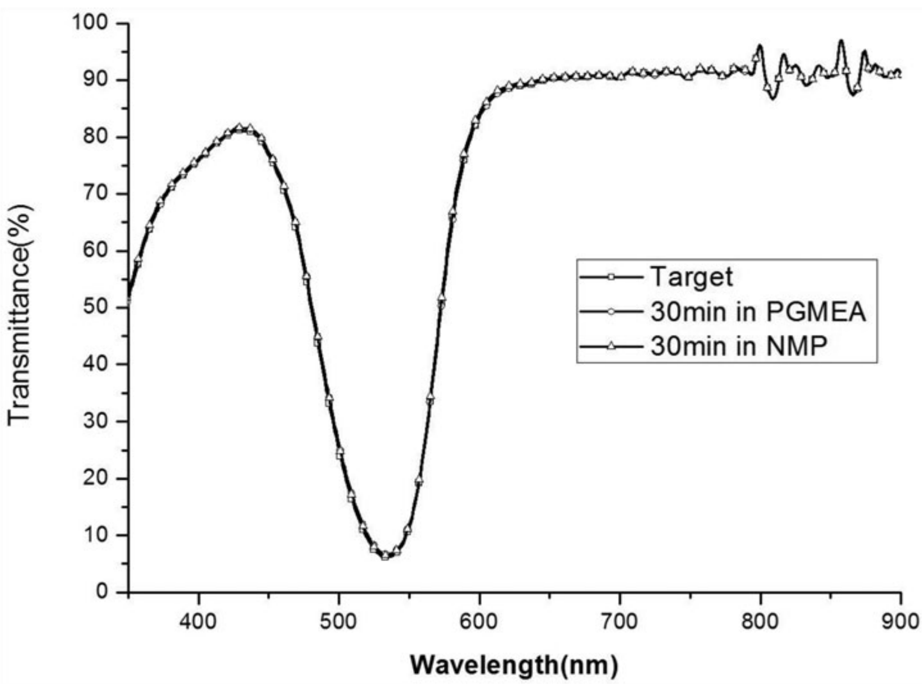


Figure 4. UV-visible transmittance spectra for chemical resistance of dimethyl-n-octylaminated acid red 289 dye (6).

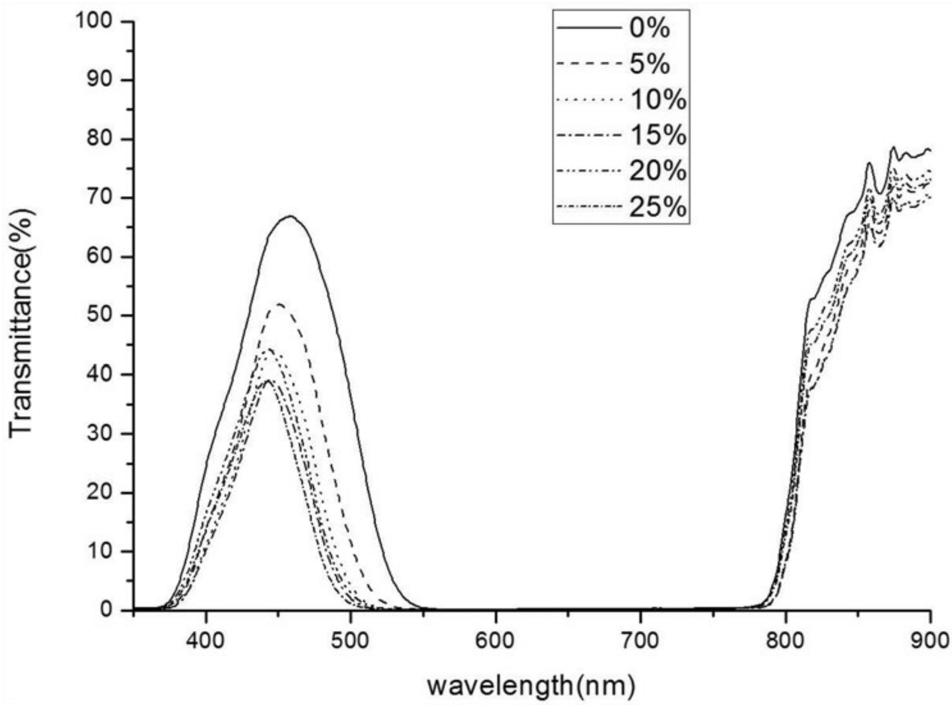


Figure 5. UV-visible transmittance spectrum of the result of the color purity improvement test.

Color resist samples were made up of increasing 5 wt.% synthetic dye against reference blue pigment 15:6 millbase. The color filter was fabricated using the same process as in our other tests. After hard-baking was completed, the color characteristics were compared to each of the other color filters. Through the CIE 1931 chromaticity diagram, we know that the color purity of the reference blue pigment color was improved. But, UV-visible transmittance spectrums in Fig. 5. were partially decreased due to aggregation of particles of pigments and dyes.

Conclusions

In this study, we designed and synthesized new acid dyes that consist of alkyl amine groups through a simple method of reaction.

These acid dyes were dissolved in organic solvents due to interrupt particle packing because of long alkyl amine groups. We fabricated color filters without the milling process to disperse pigment particles. However, one problem was thermal stability. Previous studies show that thermal resistance, light, and chemical stabilities of dye-based CF are restricted to commercial production and application of LCD color filters. Therefore, we tested thermal stability using the TGA and the UV-visible transmittance spectrum.

TGA proved that dimethyl-n-octylaminated acid red 289 dye was stable at 230°C by a result of below 3% weight loss. Over 300°C, this dye withstood this high temperature. In addition, the colored films made out of synthesized aminated acid dyes exhibited adequate resistance to strong polar organic solvents. The chromatic change (ΔE_{ab}) was less than 3, indicating very good chemical stability.

Acknowledgment

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