

Preparation of Colour Filter Photo Resists for Improving Colour Purity in Liquid Crystal Displays by Synthesis of Polymeric Binder and Treatment of Pigments

Chun Yoon* and Jae-hong Choi†

Department of Chemistry, Sejong University, Seoul 143-747, Korea. *E-mail: chunyu@sejong.ac.kr

†Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, Korea

Received May 04, 2009, Accepted July 03, 2009

Liquid crystal display (LCD) devices contain a colour filter which can visualise colour images by transmitting or absorbing light. Colour properties of LCD mainly depend on colour materials such as pigments and polymeric binders. In this paper, colour properties were studied to improve colour quality of LCD. Generally, the colour properties can be classified into three categories which are colour purity, brightness and contrast ratio. For this study, photo resists were prepared by treatment of pigments and synthesis of polymeric binder. The treated pigments were dispersed and formulated with additives for preparing a photo resist that could be used for manufacturing colour filters. As a result of what we studied, type, mixture ratio and concentration of pigments were very important to improve colour purity of LCD device.

Key Words: Pigments, Liquid crystal displays, Colour purity, Photo resist, Colour coordination

Introduction

LCD is composed of two main parts; a colour filter and a thin film transistor circuit board.¹ In the image processing of LCD device, the role of the colour filter is the most important in terms of the colour properties that can be classified into three categories: colour purity (colour strength and colour representation), contrast ratio and brightness. In this paper, the focus will be the colour purity among the colour properties.

The colour filter consists of red, green and blue colour pixels that are prepared by coating a photo resist that contains polymeric binder and pigments.^{2,3,4} The grade of HDTV generally requires a highly functional colour filter with colour purity of around 72%, while mobile and monitor grades need colour filters with

colour purity of around 45% and 60%, respectively, based on NTSC standard, shown in Figure 1.⁵

Red, green and blue, three primary colours for colour filters, are produced by the various pigments.⁶ Suitable selection of pigment is significant to make the colour filter show excellent colour purity, brightness and contrast ratio. Higher concentration and mixture ratio of pigment are required to get higher colour purity, but brightness is in inverse proportion to the concentration. Introduction of pigment had overcome the drawbacks of dyes, but problems of poor colour purity and contrast ratio existed at early stage.^{7,8,9}

Colour purity can be assessed by CIE Yxy chromaticity. The Y value is brightness, while the x and y values are colour coordinates on the CIE 1931 colour chromaticity diagram. The percent value of colour purity as a triangle area can be calculated based on the NTSC standard; the bigger triangle implies higher colour purity as shown in Figure 1. We will discuss how the colour purity can be improved by type, mixture ratio and concentration of pigments. We will discuss how the colour purity can be improved by type, mixture ratio and concentration of pigments.

Experimental Section

Equipments. Data of colour property and transmittance spectra were measured using an MCPD 3700 (Otsuka electronics, Japan). A spin-coater (Sungwon electronics, Korea) was used for coating of CFPR on glass substrates. Particle size of pigments was recorded on a particle size analyser (Par III, Otsuka Electronics, Japan). Thickness of coated materials on glass was measured using a profiler (alpha-step IQ, KLA-tencor, USA). A photo mask aligner (MDE-400, Midas system Co., Ltd., Korea) was used for UV-curing of CFPR. The percent value of colour purity was calculated using the colour gamut calculator (CGC-Ver. 3.1) software.

Materials. The pigments used in this study were CI Pigment

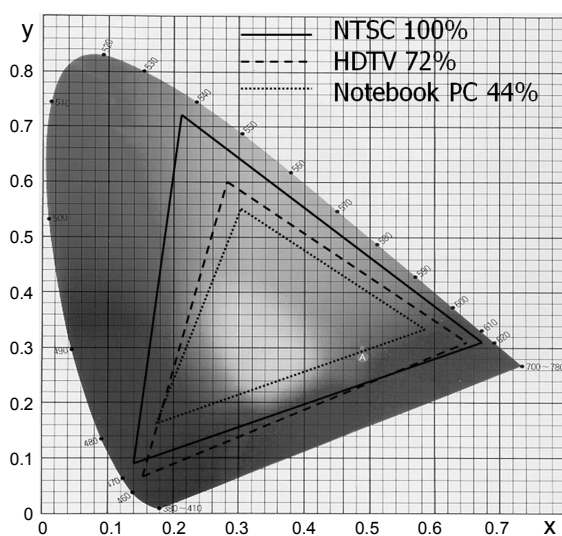


Figure 1. CIE 1931 chromaticity diagram and typical colour purity of LCD devices.

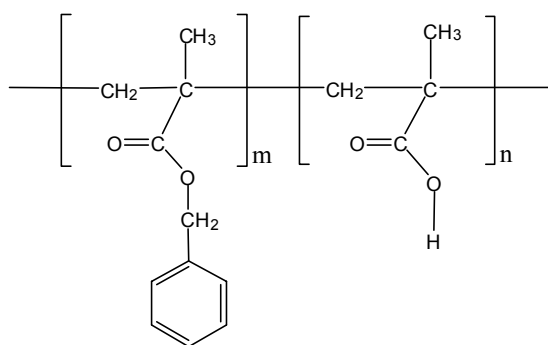


Figure 2. Structure of the polymer containing carboxylic acid group for alkali development.

Red 254 (Irgaphore Red BT-CF, Ciba specialty Chemical, Switzerland), CI Pigment Green 36 (Fastogen Green 2YK, Dai Nippon Ink and Chemicals, Japan), CI Pigment Blue 15:6 (Fastogen Blue EP-169, Dai Nippon Ink and Chemicals, Japan), CI Pigment Red 177 (Chromophtal Red A2B, Ciba Specialty Chemicals, Switzerland), CI Pigment Violet 23 (Hostperm Violet RL COF, Clariant, Switzerland), and CI Pigment Yellow 150 (Yellow Pigment E4GN-GT, Yamamoto trading, Japan).

Glass (370 mm × 470 mm × 0.63 T, 5 K Super) used as a coating substrate in this study was manufactured by Samsung Corning Precision Glass Ltd (Korea). The glass used was cut into suitable fragments (5 cm × 5 cm) for coating tests.

The dispersants, Disperbyk 163 and 2001, used for grinding pigments were manufactured by BYK-chemie (Germany).

Chemicals for a preparation of a colour filter photo resist included dipentaerythritol penta-/hexa-acrylate as a multi-functional monomer, supplied from Aldrich Chemicals (USA); Irgacure-369 as a photo initiator, supplied from Ciba Specialty Chemicals; and FC-4432 as a surfactant, supplied from 3M Company (USA). A binder for the colour filter photo resist was synthesised using benzyl methacrylate and methacrylic acid, supplied from Aldrich chemicals (USA).

Preparations of pigment pastes. CI Pigment Red 254 paste: 15 g of the CI Pigment Red 254 was stirred with 15 g of a dispersant (Disperbyk 163, active ingredient 45%) and 70 g of PGMEA (propylene glycol methyl ether acetate, Aldrich chemicals, USA) for about an hour of wetting process. The mixture was ground with 300 g of zirconia beads (diameter: 0.5 mm) in a plastic vessel (diameter: 7.5 cm; height: 15 m) for 5 hours. A gear-shaped agitator (diameter: 5 cm) was employed, and the rotation speed was about 2500 rpm. The pigment paste was cooled to 15 ~ 20 °C using an ice water bath during grinding. The beads were filtered off using a sieve to collect pigment paste. Particle size analysis showed that the mean particle size was around 74 nm.

CI Pigment Green 36 paste: 15 g of the Pigment Green 36 and 0.75 g of CI Pigment Yellow 150 were stirred with 20 g of a dispersant (Disperbyk 2001, active ingredient 46%) and 65 g of PGMEA for about an hour of wetting process. Small amount of the yellow pigment was used as a synergist to increase milling efficiency and stability. The pigment was ground for preparing a paste using the same method described for CI pigment Red 254. Particle size analysis showed that the mean

particle size was around 76 nm.

CI Pigment Blue 15:6 paste: 15 g of the CI Pigment Blue 15:6 were stirred with 15 g of a dispersant (Disperbyk 163, active ingredient 45%) and 140 g of PGMEA for about an hour of wetting process. The pigment was ground for preparing a paste using the same method described for CI Pigment Red 254. Particle size analysis showed that the mean particle size was around 81 nm.

CI Pigment Red 177 paste: 15 g of the CI Pigment Red 177 was stirred with 20 g of a dispersant (Disperbyk 2001, active ingredient 46%) and 65 g of a PGMEA for about an hour of wetting process. The pigment was ground for preparing a paste using the same method described for CI Pigment Red 254. Particle size analysis showed that the mean particle size was around 68 nm.

CI Pigment Violet 23 paste: 15 g of the CI Pigment violet 23 was stirred with 15 g of a dispersant (Disperbyk 163, active ingredient 45%) and 70 g of PGMEA for about an hour of wetting process. The pigment was ground for preparing a paste using the same method described for CI Pigment Red 254. Particle size analysis showed that the mean particle size was around 87 nm.

Pigment Yellow 150 paste: 15 g of the CI Pigment Yellow 150 was stirred with 20 g of a dispersant (Disperbyk 163, active ingredient 45%) and 65 g of PGMEA for about an hour of wetting process. The pigment was ground for preparing a paste using the same method described for CI Pigment Red 254. Particle size analysis showed that the mean particle size was around 74 nm.

Synthesis of poly(benzyl methacrylate-co-methacrylic acid). Methacrylic acid (6.9 g, 0.08 M) and benzyl methacrylate (33.1 g, 0.19 M) were stirred in 60.0 g of PGMEA under nitrogen purging to expel oxygen. The polymerization was carried out at 90 °C for 5 hours using 2.0 g of 2,2'-azobisisobutyronitrile (Junsei chemicals, Japan) as a radical initiator. Polymer content was calculated by drying a small amount of the mixture in oven at 200 °C. Viscosity of the polymer mixture was about 368 cP at 25 °C, and polymer content was about 37%. The GPC data of the polymer show weight and number average molecular weight 17,776 g/mol. The polymer synthesised was used as a binder solution without isolation. The value of m and n of the polymer structure represents 7 and 3 respectively in Figure 2.

Preparation of a colour filter photo resists (CFPR). 40.0 g of the pigment paste, 13.5 g of the binder solution, 5.0 g of dipentaerythritol penta-/hexaacrylate, 1.0 g of Irgacure-369 and 0.1 g of FC-4432 were mixed with 40.4 g of PGMEA. This mixture was stirred for 1 hour in a dark room. After stirring, the mixture was filtered using a membrane PTFE (porosity 1.0 μm) filter and ensured not to be exposed to light. The pigment mixture ratio of each formulation is listed in Table 1.

Preparation of test glass sheets. A small glass sheet (5 cm × 5 cm) was coated with the prepared photo resists by a spin coater at 350 rpm, 550 rpm, 700 rpm, 850 rpm and 1000 rpm, respectively, for 10 seconds to control thickness of thin layer. The coated glass was pre-baked to evaporate solvent at 80 °C for 90 seconds. UV exposure was carried out without a photo-mask on 200 mJ/cm² of strength at 360 nm. The development process for generating pixels was skipped, and the post-bake

Table 1. Pigment mixture ratio in CFPR

	Formulation No.	Mixture ratio of pigment paste
Red	R1	Red 254 100%/Red 177 0%
	R2	Red 254 95%/Red 177 5%
	R3	Red 254 90%/Red 177 10%
	R4	Red 254 85%/Red 177 15%
	R5	Red 254 80%/Red 177 20%
Green	G1	Green 36 70%/Yellow 150 30%
	G2	Green 36 65%/Yellow 150 35%
	G3	Green 36 60%/Yellow 150 40%
	G4	Green 36 55%/Yellow 150 45%
	G5	Green 36 50%/Yellow 150 50%
Blue	B1	Blue 15:6 100%/Violet 23 0%
	B2	Blue 15:6 95%/Violet 23 5%
	B3	Blue 15:6 90%/Violet 23 10%
	B4	Blue 15:6 85%/Violet 23 15%
	B5	Blue 15:6 80%/Violet 23 20%

process was followed for 30 minutes at 220 °C.

Each test glass sheet was measured for evaluating CIE Yxy value by an MCPD-3700 instrument.

Thickness of thin film on test glass sheet was recorded using an alpha-step IQ instrument.

Results and Discussion

As previously discussed, type and mixture ratio of pigments are essential to achieve better colour purity of the colour filter of LCD. Thus, CI Pigment Red 254, CI Pigment Green 36 and CI Pigment Blue 15:6 are suitable for main colours, whereas CI Pigment Red 177, CI Pigment Yellow 150 and CI Pigment Violet 23 are useful as mixing colours.

The typical spectrum of CCFL shows that the central peak value of each colour, red, green and blue is around 611 nm, 544 nm and 440 nm respectively.¹⁰ The amplitude width and central peak values are unalterable in the case of using typical phosphors; however, the degree of lighting intensity can be controlled by adjusting the proportion of R, G, and B phosphors.¹¹

A single or a mixture of pigment paste was added to be 6% concentration of pigment to the final photo resist. The amount of other ingredients in the final photo resist composition was about 2.7% of dispersant, about 5% of multifunctional monomer, about 5% of binder polymer, about 0.1% of fluorosurfactant, about 1.0% of UV curing agent, and with the remainder being PGMEA solvent.

The transmittance spectrum of CI Pigment Blue 15:6 is shown in Figure 3. The central peak appeared at 450 nm which is suitable for filtering the visible region except blue. Additionally, the mixture of CI Pigment Blue 15:6 and CI Pigment Violet 23 showed a narrower and lower transmittance band compared to that of CI Pigment Blue 15:6 alone, which resulted in higher colour purity.

CI Pigment Violet 23 is suitable as a mixing component to increase the colour purity; however, quantity of the violet pigment should be regulated by regarding deviation of colour target and decrease of brightness.

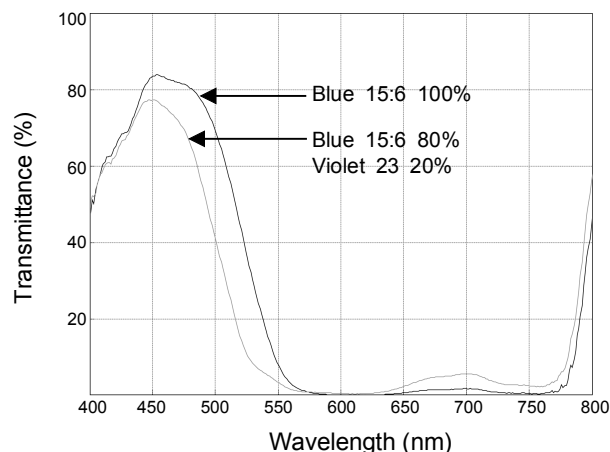


Figure 3. Transmittance spectrum of pure blue and mixture blue, mixing of pigment shows narrower transmittance band increasing colour purity.

Table 2. Typical colour coordinate values of blue CFPR on test glass sheets

Formulation	rpm	Y	x	y	Thickness (μm)
B1	350	10.351	0.13272	0.10595	2.45
	1000	23.323	0.14137	0.16817	0.95
B5	350	3.4080	0.14264	0.05181	2.54
	1000	11.119	0.14488	0.10210	1.01

The typical coordinate values of the mixed and single pigments analysed by varying the thickness are listed in Table 2. The mixtures of blue and violet pigments exhibited much smaller y values as a result of higher colour purity compared to that of blue pigment alone. For example, the formulation B1 which consisted of CI Pigment Blue 15:6 only showed 19.70 for the Y value, 0.13686 for the x value and 0.15175 for the y value at 1.21 μm thickness. Whereas, the B5 formulation, which consisted of 80% of CI Pigment Blue 15:6 and 20% of CI Pigment Violet 23, showed 8.502 of Y value, 0.14181 of x value and 0.08671 of y value at similar thickness 1.25 μm. This example also shows that the Y value as a brightness decreases very much by the addition of violet pigment.

It was found, as listed in Table 2 that the B5 formulation gave much smaller y values resulting in better colour purity, while the B1 formulation generally gave bigger y values resulting in better brightness. Consequently, addition of CI Pigment Violet 23 is a very useful method to decrease the y value for the purpose of improving colour purity. All measuring data of each formulations is represented by an excel drawing in Figure 4, it shows clearly the relationships between mixture ratios and colour coordination values depending on thickness.

With an increase in violet pigment, y value decreases rapidly, as shown in Figure 4. Therefore, it was concluded that the B1 formulation can not practically provide y value under 0.08, which is required for HDTV devices. In this case, the B5 formulation would be the best choice to achieve these colour coordinate values.

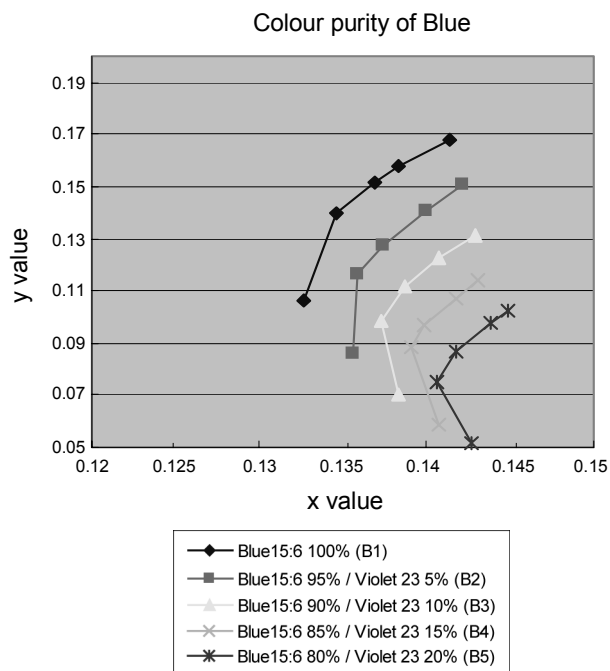


Figure 4. Relationship between x value and y values depending on mixture ratio (in blue).

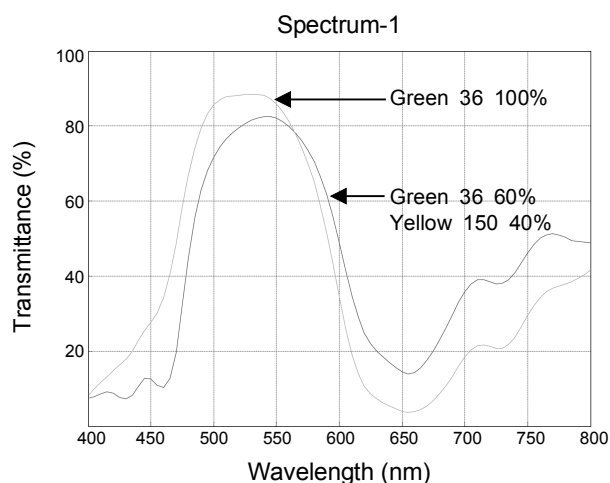


Figure 5. Transmittance spectrum of pure green and mixture of green, mixing of pigment shows narrower transmittance band increasing colour purity.

By considering these results, CI Pigment Blue 15:6 alone is suitable for mobiles and notebook PCs which prefer brightness rather than colour strength. The mixture of CI Pigment Blue 15:6 and CI Pigment Violet 23 is suitable for monitors and TVs which require high colour purity. Thus, LCD manufacturers can choose an adequate mixture ratio of blue and violet for their target devices.

CI Pigment Green 36 was used as a main colour for preparation of green pixel, but the green pigment would not be used alone because of its high transmittance of blue region under 460 nm as shown in Figure 5. Therefore, the yellow pigment for mixing was required to absorb blue region leading to increase in colour purity. CI Pigment Yellow 150 is generally used as a mixing colour

Table 3. Typical colour coordinate value of green CFPR on test glass sheets

Formulation No.	rpm	Y	x	y	Thickness (μm)
G1	350	53.487	0.28524	0.59354	2.56
	850	70.835	0.31347	0.49856	0.99
	1000	72.594	0.31555	0.48891	0.92
G5	350	59.130	0.31799	0.58647	2.50
	1000	76.045	0.34576	0.51106	0.99

for green shade. Addition of yellow pigment shifts the central peak of transmittance to the longer wavelength as shown in Figure 5. This shift can avoid overlap of blue colour transmittance as a result of giving higher purity of green colour.

Colour coordinate values of each formulation of green are listed in Table 3. A higher y value represents a more greenish colour, and a higher x value represents a more yellowish colour. Both colour coordinate values, x and y, tend to be higher with an increase in quantity of CI Pigment Yellow 150. For example, the G1 formulation which consisted of green 70% and blue 30% showed 70.835 of y value, 0.31347 of x value and 0.49856 of y value at 0.99 μm of thickness, whereas the G5 formulation which consisted of 50% of green and 50% of yellow showed 76.045 of Y value, 0.34576 of x value and 0.51106 of y value at the same thickness, 0.99 μm . It can be explained that the increase in yellow pigment provides a higher x value, higher y value and higher brightness at same pigment concentration leading to the improvement in colour purity. However, as with the result in blue colour, the quantity of yellow pigment should be regulated depending on the deviation of target.

Another interesting aspect is that the y value could be improved considerably by an increase of coating thickness in the same formulation. For example, the y value of the G1 formulation represents 0.48891 at 0.92 μm and 0.59354 at 2.56 μm . This situation clearly indicates that coating thickness as a concentration of pigment is a critical parameter to achieve a higher colour purity of green.

As shown in Figure 6, it was impossible to get the coordinate values such as 0.32 for x value and 0.57 for y value by using the G1 formulation. In this case, the G4 or G5 formulations were suitable to achieve these coordinate values. It was also found in this experiment that the ratio of mixture and concentrations of pigment were important to achieve optimum target values in green shades.

In terms of brightness, unlike blue colour, brightness Y value increased upon the addition of yellow pigment as a mixing colour, owing to the high brightness of the yellow pigment.

CI Pigment Red 254 was used as a main colour for preparation of red pixel. The red pigment can be used alone or together with CI Pigment Red 177. The maximum transmittance observed around 650 nm for CI Pigment Red 254 and 670 nm for CI Pigment Red 177 is shown in Figure 7. CI Pigment Red 177 produced deep red colour, while CI Pigment Red 254 produced bright red colour. For this reason, the combinations of these red pigments are needed for the appropriate target value.

The coordinate values of the mixed and sole red pigments

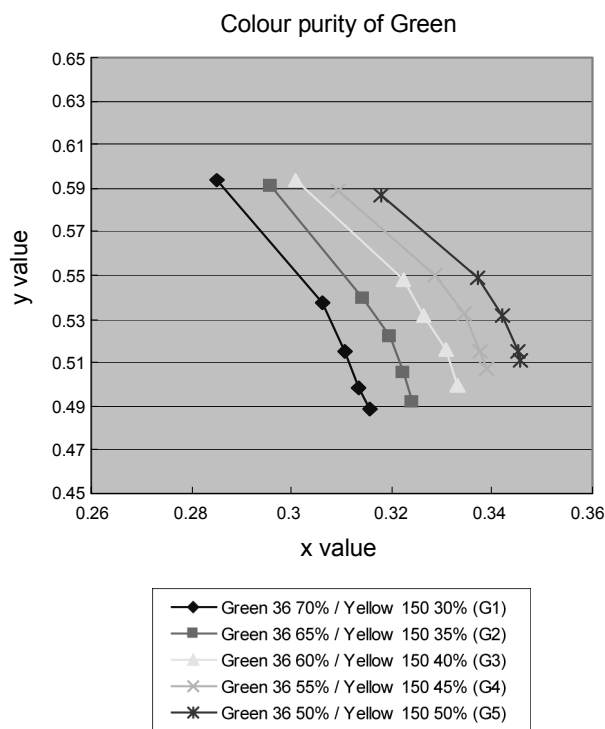


Figure 6. Relationship between x value and y value depending on mixture ratio (in green).

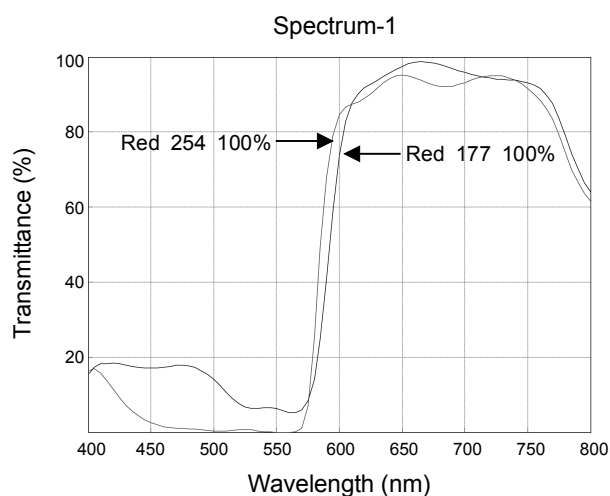


Figure 7. Transmittance spectrum of CI Pigment Red 254 and Red 177, mixing of pigment shows shifted transmittance band increasing colour purity.

Table 4. Typical colour coordinate value of red CFPR on test glass sheets

Formulation No.	rpm	Y	x	y	Thickness (μm)
R1	550	23.743	0.62566	0.32885	1.82
	1000	27.080	0.57143	0.31314	1.17
R5	550	21.703	0.63252	0.32386	1.86
	1000	25.689	0.56836	0.30826	1.23

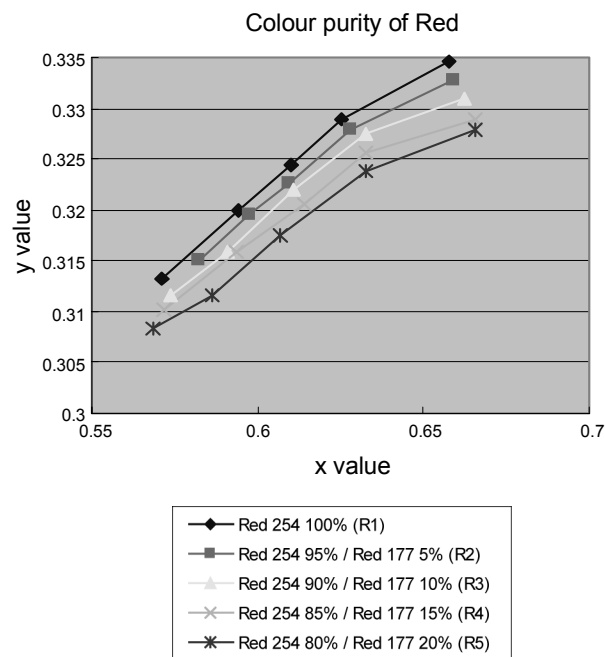


Figure 8. Relationship between x and y values depending on mixture ratio (in red).

with a variety of thickness are listed in Table 4, which produces a clear trend that the mixtures of CI Pigment Red 254 and CI Pigment Red 177 gave smaller Y value, bigger x value and smaller y value as a result of higher colour purity compared to that of CI Pigment Red 254 only. Another interesting aspect of red colour was that the y value and the Y value decrease continually with an increase in quantity of CI Pigment Red 177, while the x value did not increase continuously and was maximised when the quantity of CI Pigment Red 177 was over 15%. Therefore, around 15% of the CI Pigment Red 177 would be the optimal quantity for increasing colour purity in red colour. As discussed above, x value generally increases with an increase of CI Pigment Red 177, while the Y value and the y value decreases. For example, the formulation R1 which consisted of CI Pigment Red 254 only shows an Y value of 23.743, an x value of 0.62566 and an y value of 0.32885 at 1.82 μm of thickness, while the R5 formulation which consisted of 80% of CI Pigment Red 254 and 20% of CI Pigment Red 177 showed a Y value of 21.703, an x value of 0.63252 and a y value of 0.32386 at similar thickness, 1.86 μm , as expected.

Figure 8 clearly shows that the addition of CI Pigment Red 177 shifted colour coordinate values to the right and down in the chromaticity diagram as colour purity increased. The R1 formulation did not provide an x value bigger than 0.65 when the y value was lower than 0.326; in this case, the R5 formulation should be employed to get these coordinate values. However, the effect of mixing with red colour was smaller compared to that of CI Pigment Violet 23 with blue colour.

It was also found that two methods were required to improve colour purity. One is to mix pigments and the other is to increase concentration of pigments as coating thickness. In the methods of mixing pigment, additional pigments such as CI Pigment Red 177, CI Pigment Yellow 150 and CI Pigment

Table 5. Combinations of formulation and their colour purity

Combination No.	Formulation No.	Colour coordination			Thickness (μm)	Colour purity (%)	Suitable device
		Y	x	y			
C1	R1	27.1	0.571	0.313	1.17	43.6	Mobiles Notebook PC
	G1	65.2	0.306	0.537	1.41		
	B1	21.2	0.138	0.158	1.17		
C2	R5	17.7	0.665	0.328	3.39	73.1	HDTV
	G3	56.1	0.300	0.593	2.59		
	B5	6.7	0.141	0.075	1.45		

Violet 23 could be used. Especially, CI Pigment Violet 23 produced the greater effect compared to CI Pigment Yellow 150 and CI Pigment Red 177. However, the use of the yellow pigment was significant because it achieved a suitable green colour for conventional CCFL back light. Because, CI Pigment Green 36 has a somewhat blue tone; thus the mixing of yellow pigment is needed to achieve a purer green colour. The use of CI Pigment Red 177 was used for adjusting the colour tone of CI Pigment Red 254 which induces a bright red, but somewhat weak, colour.

Table 5 shows the combinations of the formulations which are suitable for each target device such as mobile, notebook PC, monitor and HDTV. As discussed before, mix and concentration of pigments are considered, but these are only examples, LCD manufacturers have their own appropriate target values. The combination C1 consisting of the formulation R1, G1 and B1 with thin coating produces a 43.6% colour purity value, suitable for displays of mobiles and notebook PC, while the combination C2 consisting of R5, G3 and B5 with thick coating produces a 73% colour purity, which is suitable for HDTV.

In this study, for clear comparison of each pigment, all formulations were prepared containing 6% of the pigments; thus, coating thickness was not uniform in high colour purity systems as listed in Table 5.

As a consequence of the experiment, to improve colour purity, increments of x value in red colour, increments of y value in green colour and decrements of y value in blue colour.

Conclusion

Authors found that CI Pigment Red 254, CI Pigment Green 36 and CI Pigment Blue 15:6 were useful for main colours, and CI Pigment Red 177, CI Pigment Yellow 150 and CI Pigment Violet 23 were useful for mixing colours. We also found that improvement of colour purity could be achieved by concen-

tration and mixture ratio of pigments. This study showed that appropriate combination of the pigments produced colour purity greater than 72% suitable for HDTV, an electronic device which preferentially uses colour purity instead of brightness. For mobiles and notebook PCs, colour purity could be achieved at around 44% without decrease of brightness. As the results of these experiments, unfortunately, increase of colour purity gives rise to decrease of brightness; we have to solve this problem with an introduction of new kinds of pigments or dyes, which give better colour purity and brightness simultaneously.

Acknowledgments. The authors wish to thank Prof. Cheon-Ho Yoon, Dept. of chemistry, Myongji University for measuring GPC data.

References

1. Kubo, M.; Fujioka, S.; Ochi, T.; Narutaki, Y.; Shinomiya, T.; Ishii, Y.; Funada, F. *Technical Digest of IDW 99'*; SID: Okata, 1999; p 183.
2. Ichimura, K. *Advanced Technologies for LCD Color Filters*; CMC Publishing: Tokyo, 2006; p 8.
3. Takahashi, T. *J. Imag. Soc. Japan* **2002**, 41, 68.
4. Sugiura, T. *J. Print. Sci. Tech. Japan* **1996**, 356.
5. Jung, I. B.; Ahn, S. H.; Nam, S. Y. *Clean Tech.* **2008**, 14, 21.
6. Ichimura, K. *Advanced Technologies for LCD Color Filters*; CMC Publishing: Tokyo, 2006; p 81.
7. Shimamura, M.; Furukawa, T.; Murakami, A.; Haga, T. *USP 4837098*; 1989.
8. Masahi, S.; Kenichi, F.; Toyoda, I.; Hirasawa, Y. *JP 2001-220520*; 2001.
9. Kunihiro, I.; Shusaburo, K.; Toshio, K.; Akira, O. *JP 60-129707*; 1985.
10. Deno, T. *Pigments for Color Filter Application in LCD (Technical Brochure)*; Ciba Specialty Chemicals, 2005.
11. Chang, C.; Kao, H. *USP 7,350,955*; 2008.