Research on the Formula of Usable Dye Color Photoresist

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Abstract

In order to save energy, it is necessary to develop dye photoresist. This article provides a detailed introduction to encountered issues and solutions by material adjustment such as polymer and monomer adjusting, providing valuable guidance for the development of dye photoresists.

Author Keywords

Dye color photoresist, color resistance layer, material composition, transmission increasing.

1. Introduction

Liquid Crystal Display (LCD) is currently the mainstream display technology in the world, with advantages such as high clarity, low power consumption, no radiation, small size, and light weight.[1] Since the first display screen was first unveiled in 1968,[2] after decades of technological iteration, LCD displays have evolved from small and simple electronic devices that can only display numbers, such as digital watches and portable calculators, to various aspects of life today, such as large-sized televisions, medium-sized laptops, tablets, car dashboards, and small-sized smartphones.[3-5]

With the gradual reduction of fossil fuels and the promotion of green environmental protection theory, the requirements for display screens are also gradually increasing, requiring more environmentally friendly production, use, and recycling. The introduction of dyes is a method to improve penetration rate, which is in line with the trend of energy conservation and environmental protection, and will enhance the competitiveness of LCDs in the display industry.[6,7] However, at present, the resources of dye photoresist (CPR) are very limited. Conducting research and development of dye CPR in advance can grasp the key formulas of dye photoresist, occupy the technological high ground, and improve product performance, which is a very important and necessary layout.

In this article, a detailed study was conducted on the formulation of a dye CPR. A series of issues encountered during the development process were systematically analyzed and improved, and ultimately, a dye CPR with parameters equivalent to pigment CPR was developed, with a penetration rate improvement of 3.55%. This article provides guidance on the formulation development of dye CPR.

2. Result and discussion

2.1 Improvement of adhesion

According to the formula of large used pigment photoresist, we set the initial formula for green dye photoresist that the polymer/monomer (P/M) is 40/60 and the green dye/yellow pigment (G/Y) is 75/25.[8-11] However, after exposure and development, we found that the color resistance layer completely peeled off from the glass substrate under the rinsing of the developer solution (figure 1a). However, when the amount of G dye was reduced to G/Y=45/55, there was only significant peeling at the center of the color resistance layer, leaving some unpeeled layer around the glass (figure 1d). Based on the test results of these two formulations, it can be clearly determined that the proportion of G dye will affect adhesion, with higher proportions resulting in poorer adhesion. At the condition of G/Y=75/25, the peeling area when P/M=60/40 is smaller than when P/M=40/60. When the P/M=80/20, there is no phenomenon of film surface peeling, indicating that the amount of resin added is also significantly correlated with the degree of peeling.

By the peeling regulation, we make three diagrams, shown in figure 2. The polar groups on the polymer, such as hydroxyl and carboxyl groups, can come into contact with the glass and adhere to it. In pigment systems, pigments are difficult to move due to their large volume and dense polymer, while the polar groups on the polymer provide sufficient adhesion to the glass. In dye systems, the fixation of dyes is achieved through interaction with the polymer, that is, by binding to the polar groups on the polymer. Therefore, at low polymer contents, the binding of dyes is reduced due to the connection of polar groups between the polymer and the glass, and the adhesion becomes weaker, making it easy for the color resist to be washed away by the developer. Increasing the proportion of polymer is an effective solution to this problem. In high resin content systems, the polar groups on the resin provide sufficient polar groups to bind with the dye, while there are also excess polar groups in contact with the glass to provide adhesion. Therefore, the P/M ratio system obtains a non-peeling color resistance layer.

2.2 Improvement of wrinkles on the surface

After solving the problem of peeling, we set P/M=80/20 and made a color resistance layer. After development, the color resistance layer was intact without any abnormalities. However, after baking at 230 ℃, some stripes can be seen on the color resistance layer under an optical microscope, as shown in figure 3a. These stripes affect the flatness of the color resistance layer and enhance light scattering during chromaticity testing, affecting the optical results.

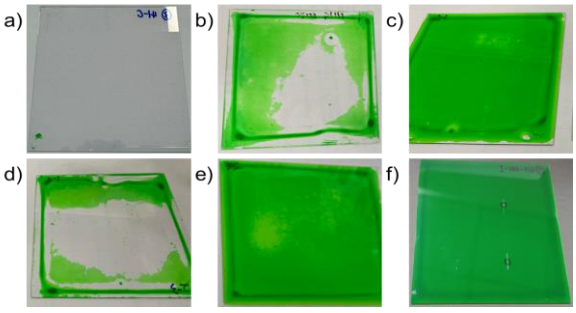

Figure 1. When the G/Y ratio is 75/25, the surface condition with P/M ratios of a) 40/60, b) 60/40, and c) 80/20, and when the G/Y ratio is 45/55, surface condition with P/M ratios d) 40/60, e) 60/40, and f) 80/20.

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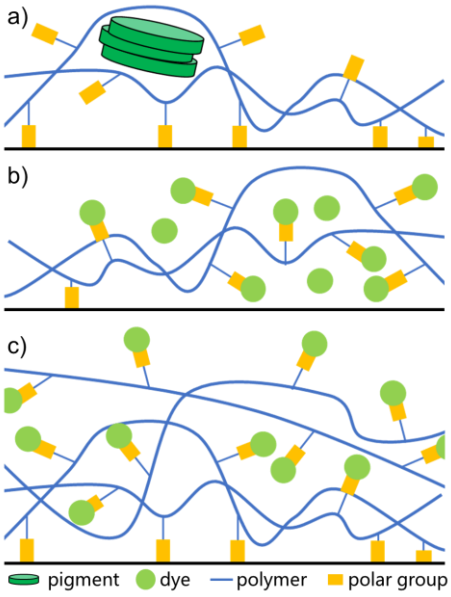

Figure 2. Schematic diagram of the relationship between polar groups and adhesion in a) pigment CPR, b) dye CPR with small amount of polymer and c) dye CPR with large amount of polymer.

Macroscopically, the stripes on the color resistance layer are distributed throughout the entire surface, and we speculate that they are mainly caused by the polymer aspect. In order to form a dense polymer film, the polymer in photoresist generally contains a large number of crosslinkable groups. During the exposure process, most of the crosslinkable groups have already been crosslinked, but there are still a small number of groups that have not been crosslinked. During the baking process, the remaining crosslinking groups will be fully crosslinked under the action of heat. The principle of color resistance layer wrinkling is shown in figure 4. Although there is no abnormality on the color resistance layer after development, during baking, the color resistance the color resistance on the surface will come into contact with air, and the oxygen in the air will be decomposed into oxygen free radicals by heat, promoting the polymer cross-linking on the color resistance layer and causing the degree of cross-linking between the color resistance layer color resistance layer and the bottom to be inconsistent, resulting in color resistance layer wrinkling. This phenomenon is not significant at low P/M ratios, but is more likely to occur at high P/M ratios. In theory, as long as the concentration of oxygen free radicals on the surface of the color resistance layer is reduced, thereby reducing the crosslinking rate likely to occur at high P/M ratios. In theory, as long as the

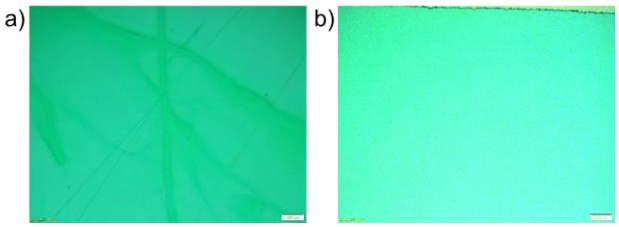

Figure 3. Optical microscope photographs of a) the surface with wrinkles and b) the surface after improvement.

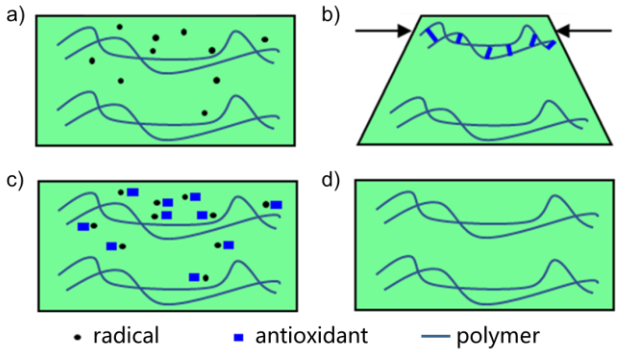

Figure 4. The G layer without antioxidant a) before oven and b) after oven, and the G layer with antioxidant c) before oven and d) after oven.

concentration of oxygen free radicals on the surface of the color resistance layer is reduced, thereby reducing the crosslinking rate of the surface, and making the surface and bottom rates roughly the same, the defect of membrane wrinkles can be eliminated. Therefore, we added antioxidant and remade the color blocking layer. After using antioxidant and baking, the color resistance layer showed good macroscopic and microscopic performance, without the problems of pigment precipitation and wrinkling. The reasons for the improvement are also shown in figure 4. Antioxidants are dispersed in various parts of the color resistance layer. During baking, oxygen free radicals generated on the surface are absorbed by the antioxidants, reducing the proportion of free radicals on the surface and ultimately solving the problem of stripes.

2.3 Improvement of development characteristics

Although dye photoresist has successfully produced entire color resistance layer, its application in display screens still requires many attempts, especially the patterned color resistance layer, in order to achieve color display on LCDs. Therefore, we need to further investigate the feasibility of patterning dye photoresists. On this basis, we modified the process conditions from exposure without a photomask to exposure with a photomask. Unexpectedly, after 120 seconds of rinsing with developer solution, the areas not exposed to UV-light still have photoresist and the glass is not revealed at all. That means the formula of dye CPR is not sufficient for use in display screens and needs improvement.

In the process of analyzing the peeling problem on the color resistance layer, we found that in order to improve adhesion, the P/M ratio was increased to a very high 80/20, which also led to the formation of a network structure in the non-exposed area where the polymer molecules tangled and knotted, reducing solubility and resulting in no significant difference between the exposed and non-exposed areas. Hence the non-exposed area was not developed to expose the glass. The proportion of polymer is very high, so the properties of the polymer have an important impact on the photoresist. The properties of the polymer in the formula can be controlled by adjusting the substituents on the side chains. Therefore, we can try to improve the development performance by optimizing the structure of the polymer. In addition to carboxyl groups, polymer side chains also have double

bonds, hydroxyl groups, and phenyl groups, among which carboxyl groups are more easily bound to alkaline developer solutions.

Therefore, we attempted to use high acid value polymers 2 and 3 instead of polymer 1, shown in figure 5. Compared to polymer 1, polymer 2's acid value increased by about 20 KOHmg/g, reaching 110 KOHmg/g, while polymer 3's acid value reached 130 KOHmg/g, while maintaining the same molecular weight. Using these two high acid value polymers to make photoresist pattern, at a development time of 60 seconds, it can be seen that as the acid value increases, the development properties do indeed improve, and the middle development area becomes larger, as shown in figure 6. From the optical microscope, there are still many photoresist residues at the edges of the pattern, indicated that this method is feasible, but it is not a complete solution to the problem.

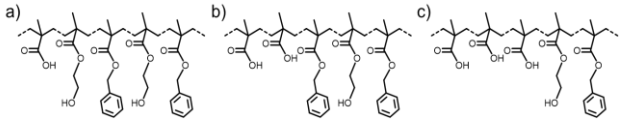

Figure 5. Structure of a) polymer 1, b) polymer 2, and c) polymer 3, where the presence of double bond groups has been ignored. In order to increase the acidity, the number of hydroxyl and phenyl groups on the side chain is reduced.

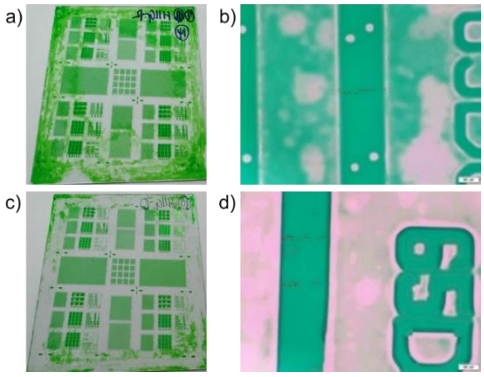

Figure 6. a) Macroscopic pattern and b) optical microscope picture of dye CPR using polymer 2. c) macroscopic pattern and d) optical microscope picture using polymer 3.

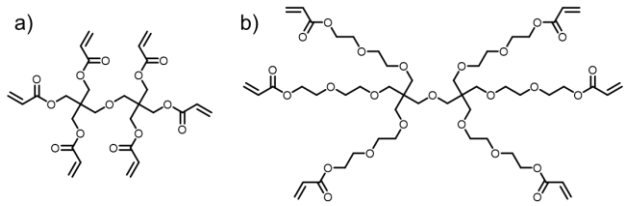

Figure 7. The structures of a) monomer 1 and b) monomer 2. Monomer 1 has a small volume, while monomer 2 contains more ether bonds, and has good hydrophilicity.

Table 1. Parameters of pigment CPR and dye CPR

Parameter	Dye CPR	Pigment CPR	Δ
Gx	0.269	0.269	0.0001
Gy	0.576	0.576	0.0001
GY	62.02	59.90	3.55%
Resolution	14	14	0
Line width (μm)	126.20	126.35	-0.15
Climbing angle (°)	57.23	56.58	0.65

We replaced the monomer to further optimize the development properties. Two types of monomer structures are shown in figure 7, with monomer 1 having a smaller volume, which can make the color resistance layer more compact; And monomer 2 has more ether bonds and better hydrophilic properties. Therefore, we use monomer 2 in the formula to address the issue of residue. The photoresist pattern is shown in figure 8a. It can be seen that after using monomer 2, there is no photoresist residue in the unexposed area, and there is also no residue inside the hole observed under a microscope. Compared with the pigment photoresist in figure 8b, some parameters of the dye photoresist are at a considerable level, and the parameters are exhibited in Table 1. It is worth noting that under the same color coordinates, the penetration rate of dye photoresist is increased by 3.55% compared to pigment photoresist. Although the increase is not significant, dye photoresist has been proven to effectively improve penetration rate and reduce energy consumption.

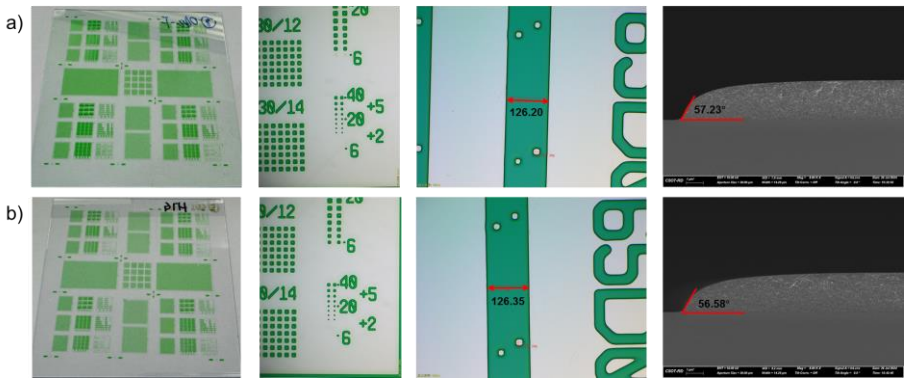

Figure 8. After changing the monomer, the pattern, line width and resolution under an optical microscope, and climbing angle data measured by SEM of a) dye CPR and b) pigment CPR.

3. Conclusion

This paper introduces the formula adjustment process during the development of a dye CPR. By adjusting the P/M ratio and introducing antioxidants, the problems of peeling and stripe on the surface were resolved. In order to achieve patterning of the color resistance layer, we adjusted the structure of the polymer and replaced the monomers in the dye CPR, so that the patterning parameters were comparable to those of the pigment CPR. And the penetration rate of the dye photoresist has increased by 3.55%. Although the improvement in penetration rate is not so high, the development of dye photoresist is an important way to achieve high penetration rate in the future. This paper provides valuable guidance for the formulation development of dye CPR and has high academic value.

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