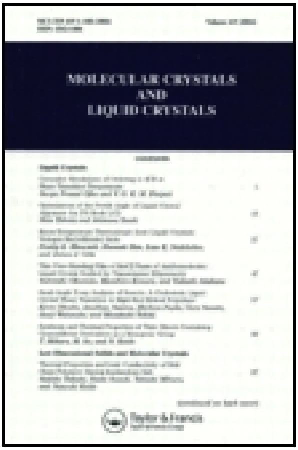

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Studies on Effects of Compatibilizers in Over Coating Layer Materials for TFT Panels

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Over coating layer (OCL) materials were prepared by mixing acrylate copolymer and epoxy compound. The shelf life of the OCL materials could be extended, because of suppression of the crosslinking reaction between the acrylic acid and epoxy groups during storage at room temperature. However, the microphase separation between the acrylate copolymer and the epoxy compound was caused during the post-baking process, leading to the formation of rough surface, and consequently decrease in the transparency. The compounds having longer alkyl chains and acid group such as palmitic acid and 2-ethylhexyl maleate were found to prevent the microphase separation.

Keywords: over coating layer; positive type photoresist

INTRODUCTION

Recently, the production and sales of liquid crystalline displays (LCDs) are increasing remarkably in Flat Panel Display market. A TFT array panel consists of many TFT devices in which the height of each TFT device is in a range of 2-3 μm. The disorder of liquid crystal molecules on the TFT devices sometimes causes a poor quality of the TFT panel. Over coating layer (OCL) materials have been widely

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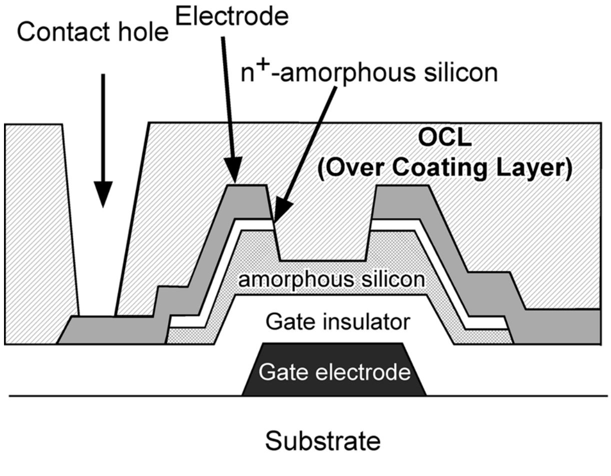


FIGURE 1 TFT LCD panel bearing OCL.

studied for the TFT panel, because the order of liquid crystal molecules can be improved by coating OCL materials on the TFT devices (Fig. 1) [1,2].

A LCD display panel with the OCL film provides clear and highly minute pictures. However, present OCL materials have short shelf life due to a crosslinking reaction between epoxy units and methacrylic acid units, because the most of the OCL materials developed have both epoxy and methacrylic acid units in a same polymer main chain as side groups. Therefore, we tried to extend the shelf life of the OCL materials by separating the acrylic acid and epoxy units in the OCL

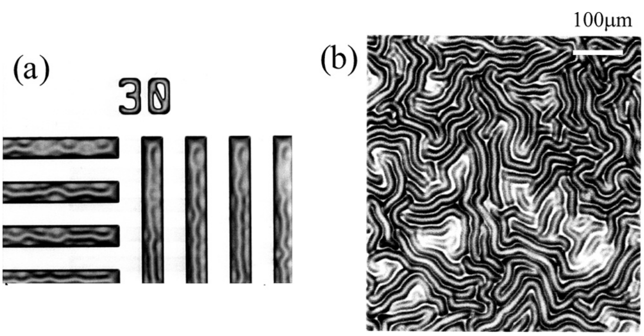


FIGURE 2 Images of rough surface of OCL film. (a) Optical microscope image (Patterned line width is 30 μm); (b) SEM image.

materials. However, the decrease in the transparency of the TFT panels was observed by using the modified OCL materials (Fig. 2). The transparency was improved by using crosslinking accelerator, but the shelf life was extremely shortened. In this study, we investigated the mechanism of the decrease in the transparency, and tried to improve the transparency without shortening of the shelf life of the OCL materials.

EXPERIMENTAL

Preparation of OCL Resist Film

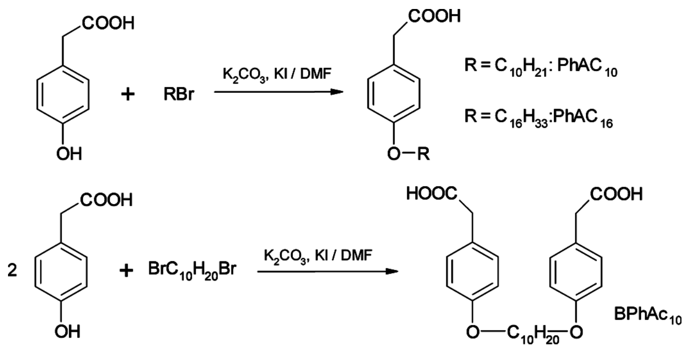
The OCL material used in this study were prepared by mixing acrylate copolymer, epoxy compound and photoactive compound, separately. The acrylate copolymer consisted of methyl methacrylate, 2-hydroxypropyl methacrylate and methacrylic acid, and its Mw was 20,000 as measured by GPC, and the monomer ratio was 57, 30 and 13 wt%, respectively. Tri-functional epoxy compound was used as the epoxy compound for crosslinking. The photoactive compound (TS-150), diazonaphthoquinone derivative, was supplied by Toyo Gosei Industries. The OCL films with a thickness of around 4.8 μm were prepared by the spin coating using propylene glycol mono methyl ether acetate (PEGMEA) as solvent on glass or silicon substrates. Soft-baking was carried out by heating at 90°C for 160 s on a hot plate.

Fabrication of OCL

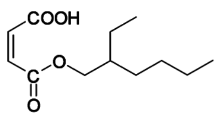
High pressure mercury lamp equipped both heat-cutting and VIS-cutting filters was used for exposure. After the exposure, the OCL films were rinsed in 0.4 wt% tetramethyl ammonium hydroxide (TMAH) aqueous solution for 80 sec. The bleaching process was carried out using high pressure mercury lamp with a heat-cutting filter. The post-baking was performed by heating in an oven at 220°C for 60 min. The final film thickness of OCL films was around 3 μm. The transmittance of the OCL films on glass was measured with a UV-VIS spectrometer (Shimadzu; UV-1600PC). The surface of the OCL films was investigated by means of optical microscope and scanning electron microscope (SEM).

Prevention Ability for Roughing

Many kinds of compounds were examined in order to prevent the surface roughing; fatty acids and their salts, alkyl amines, alkyl amides,



(a) Designed and synthesized compatibilizers.



(b) Compatibilizer having bulky chain and double bond..

FIGURE 3 Compatibilizers having both of carboxyl group and alkyl chain.

sulfonic acid, aromatic acids, surfactants and esters. Each compound was added in the OCL material, and the transparency of the OCL materials was examined by the same manner as described above.

Synthesis

Compounds having both long alkyl chain and carboxyl group were synthesized via Williamson's reaction as shown in Figure 3. All reagents used in the synthesis were purchased and used without further purification. The compounds synthesized were added to the OCL material, and examined for the enhancement of the transparency.

RESULTS AND DISCUSSION

The transparency is one of the important parameters, and transmittance higher than 90% at 400 nm is required for the OCL film with 3 μm. But the transmittance of the OCL films made by the above formulation without any crosslinking accelerator was less than 20%. Microscopic observations revealed that the low transmittance was arose from the formation of rough surface of the OCL films (Fig. 2). Actually, the corrugation with a height of 20 nm was observed by atomic force microscope [3]. In addition, the transmittance of the

OCL films was improved by coating the acrylate copolymer solution on the rough surface area of the OCL films, increasing the light transmittance of OCL film from 20% to 90%. These results indicate that the rough surface was caused only at top surface of the OCL films, and the rough surface was due to a micro phase separation of main acrylate copolymer and epoxy compound during the processes.

To prevent the microphase separation, many kinds of compounds were added to the OCL materials. As given in Table 1, only fatty acid was found to exhibit significant preventing ability for surface roughing of the OCL films. To evaluate in detail the effects of the fatty acids, some fatty acids and ester derivatives having different alkyl chains were examined. All ester derivatives used did not show any prevention effect as given in Table 2. Contrary to the ester derivatives, the fatty acids prevented the decrease in the transparency. In particular, the prevention effect of the fatty acids with longer alkyl chains was higher than those with shorter alkyl chains. Both palmitic acid and stearic acid provided clear OCL films after post-baking process by adding even at 3.9×10^{-2} M in the OCL film, whereas the OCL film added with lauric acid or myristic acid was cloudy. From the point of solubility in PGMEA and thermal stability, the lower concentration of the fatty acid may be favored. The shelf life of novel OCL material containing palmitic acid was longer than one month at room temperature.

Based on the results, it is assumed that combination of long alkyl chain with carboxyl group is important for preventing ability of the microphase separation in the OLC materials. That is, the fatty acids

TABLE 1 Prevention Abilities for Roughing of Various Types of Compounds

Type of added compound	Compound	Condition of OCL film	
		0.039 M	0.12 M
Fatty acid	Stearic acd	clear	clear
Fatty acid salt	Sodium acetate	cloudy	cloudy
	Sodium ocylate	cloudy	cloudy
Ester	Hexyl acetate	cloudy	cloudy
Alkyl amine	Octyl amine	insoluble	insoluble
Alkyl amide	Octadecane admie	insoluble	insoluble
Sulfonic acid	Benzosulfonic acid	cloudy	cloudy
Aromatic acid	Benzoic acid	cloudy	cloudy
	Phthalic acid	cloudy	cloudy
	Terephthalic acid	cloudy	cloudy
Surfantant	CTAB	cloudy	clear
	SDS	cloudy	cloudy

TABLE 2 Prevention Abilities for Roughing of Esters and Fatty Acids

Compound	Conc. in OCL film ($\times 10^{-2}$ M)	Surface condition of OCL film	Solubility in resist at 5°C
Octyl acetate	12	cloudy	cloudy
Ethyl octylate	12	cloudy	cloudy
Amyl octylate	12	cloudy	cloudy
Methyl stearate	12	cloudy	good
Ethyl stearate	12	cloudy	good
Methyl laurate	12	cloudy	good
Ethyl laurate	12	cloudy	good
Lauric acid	3.9	cloudy	good
	12	clear	good
Myristic acid	3.9	cloudy	good
	12	clear	good
Palmitic acid	3.9	clear	good
	12	clear	good
Stearic acid	3.9	clear	good
	12	clear	separated

having longer alky chains act as a compatibilizer for the system of the acrylate copolymer and the epoxy compound. In order to develop the compatibilizer with higher prevention ability as well as longer shelf life, compounds having both carboxylic acid and longer alkyl chain

TABLE 3 Prevention Abilities for Roughing of Synthesized Compounds

Compound	Conc. in OCL film ($\times 10^{-2}$ M)	Surface condition of OCL film	Solubility in resist at 5°C
Benzoic acid	0.39	cloudy	good
	3.9	cloudy	separated
Palmitic acid	0.39	cloudy	good
	3.9	clear	good
	12	clear	good
PhAc-10	0.39	cloudy	good
	3.9	clear	good
PhAc-16	0.39	cloudy	good
	3.9	clear	good
BPhAc-10	0.39	cloudy	good
	3.9	clear	good
2-Ethylhexyl maleate	0.39	clear	good
	3.9	clear	good
	12	clear	good

in a molecule were synthesized from *p*-hydroxy phenylacetic acid (Fig. 3(a)). The prevention abilities of the compounds were given in Table 3. PhAc-10 and BPhAc-10c showed better prevention ability than benzoic acid. However, the prevention abilities of the compounds were not so high compared to fatty acid such as palmitic acid. We assumed that the insufficient abilities were due to the presence of benzene ring. Thus, 2-ethylhexyl maleate was examined, because it has carboxyl group, branched bulky alkyl chain, and double bond. As given in Table 3, 2-ethylhexyl maleate showed good preventing effect on the decrease in the transparency. Bulkiness is one of factors influencing compatibilization of the acrylate copolymer and the epoxy compound. In addition, the shelf life of the OCL materials containing 2-ethylhexyl maleate was longer than one month.

CONCLUSIONS

The OCL materials showing long self life were prepared by mixing separately acrylic acid group and epoxy group. However, the microphase separation between the acrylic copolymer and the epoxy compound was brought about by the post-baking process, causing the formation of rough surface of the OCL materials, and decrease in the transparency. The compatibilizers having acid group and longer chains such as palmitic acid and 2-ethylhexyl maleate, were found to prevent the formation of the rough surface of the OCL material. The hydrophobicity, bulkiness and acid group are important for the compatibilization of the acrylic acid and the epoxy compounds.

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