Photosensitive Electrode Paste Formulation and Its Effect on Photolithographic Process

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Abstract

Photosensitive electordes(Ag and Black) are widely used in the patterning of both address and bus electrodes on the rear and front panel of plasma display panel (PDP). As the need for high resolution(>XGA) and large area(>60 inches) PDP is increased, basic understanding of each component of formulation on the photolithographic process of patterning electrodes are required in order to increase the yield in the production of PDP. In this work, the materials and amount of necessary components of photosensitive electrode paste and their effect on the photolithographic process of patterning electrodes were studied.

1. Introdution

Both address and bus electodes of PDP are patterned using photosensitive electrode paste. The process involves screen printing of the paste, drying, UV exposure, development, and sintering of the patterned electrode. The basic components of photosensitive electrode paste consist of inorganic (Ag) and organic part. The organic part include binder polymer, solvent, multifunctional monomers, photoinitiator and additives. The organic part, so called phtosensitive vehicle, has effect on the major photolithographic process such as UV exposure and development in addition to the initial screen printing and final sintering process. The important requirement of photosensitive electrode paste for PDP are shown in Table 1.

Table 1. Process Requirement of Photosensitive Electrode Paste.

Stage	Property	Specification
(1) Paste	Binder polymer Coating method Development Sintering Viscosity	Acrylic copolymer Screen printing Aqueous(alkanine)soln 550 – 580℃, 30min less than 50,000cps
(2) Exposure	Light source Dose Resolution	UV (~ 365nm) 300 ~ 500 mJ/㎠ less than 50 ㎛
(3) Electrode	Thickness (after sintering) Sheetresistance Edge curl Edge bump	5~6㎛ 6.0mΩ/□/5㎛ less than 1㎛ less than 4㎛

2. Experimental

2.1 Materials

Hydroxypropyl cellulose(Aldrich Chemical Co., MW 80,000) which is soluble in water was used as a cobinder polymer for absorbent layer paste. 3-Methoxy-3-methyl butanol(3MMB) was used as solvent(T_b = 175℃) to dissolve HPC binder polymer. UV curable monomers tested include pentaerythritol triacrylate(PETA), trimethylolpropane triacrylate(TMPTA), trimethylolpropane ethoxytriacrylate(TMPEOTA)

and other UV oligomers. Photoinitiator(HSP188) was purchased from SK-UCB Co. and used as received. Poly(methylmethacrylate -co-methacrylic acid), Poly(MMA-co-MAA), was synthesized by free radical polymerization as a aqueous alkaline solution developable binder polymer. Silver powder(Mitsui Metal Co.) samples had mean diameter of 0.8 ㎛. Dielectric powder was obtained from Daejoo Co.(T-015) for the formation of inorganic binder layer between silver film and glass substrate.

2.2 Photosensitive Electrode Paste.

Binder polymer (or mixture of polymer)was dissolved in organic solvent. To this solution was added the multifunctional monomers and oligomers and photoinitiator including additives such as dispersant, leveling agent, and wetting agent to give photosensitive vehicle. Silver powder was added to this solution and then the whole mixture was mixed well with mechanical stirrer and finally in the three roll mill.

2.3 Photolithographic Process.

The photosensitive electrode paste was coated on the clean glass substrate with screen printer and the dried in the infrared(IR) oven at 110℃ for 10-15min. The silver paste coated glass was set in the UV exposure unit and irradiated for certain period of time through the mask. The patterned sample was then developed with 0.3-0.5wt% KOH solution, the electrode patterned glass was sintered in the electric oven upto 560℃ for 30min. The resulting electrode pattern was examined with the optical microscope and its resistance was measured. This process is shown graphically in Fig.1.

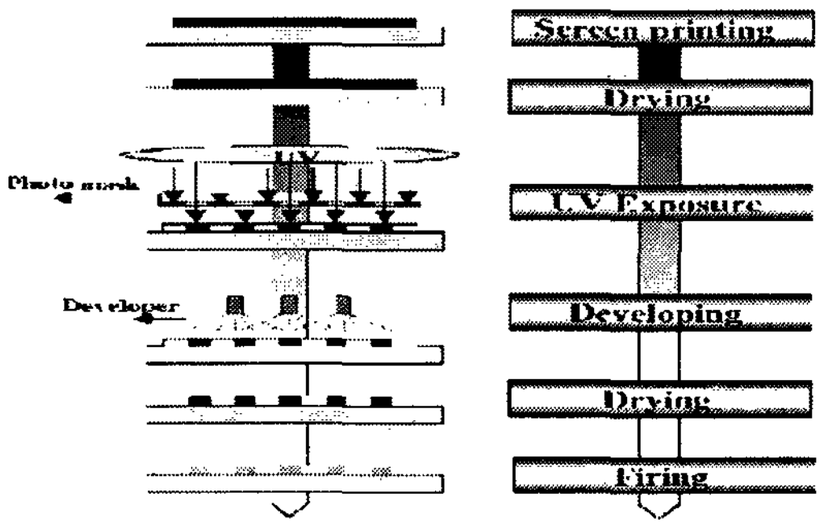


Fig.1. Photolithographic patterning of silver electrode for PDP

3. Results and Discussion

3.1 Component and Formulation of Electrode Paste.

A preliminary formulation of photosensitive silver paste is shown in Table 2. From Table 2 the ratio of photomonomer to binder polymer was found to give adequate screen printing and photolithographic property in the range of 130~150%. Solvent also affects the viscosity and drying property of the paste. Texanol gave good screen printing property and relatively short drying time as shown in Table 2. The 3-roll mixing time of the paste strongly affected the rheological property of the paste as shown in Fig.2

Table 2. Basic Formulation of Photosensitive Ag Paste

No	BP (g)	Sol (g)	PM (g)	PI (g)	Ag (g)	Gf (g)
ACP-5	5	5.5 (TX)	7.5	0.4	27.4	0.83
ACP-6	5	5.5 (TX)	5	0.4	23.1	0.67
ACP-7	5	5.5 (TX)	2.5	0.4	21	0.64
ACP-8	5	6.5 (TX)	2.5	0.4	27.4	0.83
ACP-9	5	4.5 (BC)	2.5	0.4	23.1	0.67
ACP-10	5	4.5 (BCA)	2.5	0.4	21	0.64

Ref)
(1)BP:acrylbinderpolymer ,(2)TX:texanol,(3)PM:photomonomer,(4)PI:Photoinitiator,(5)Gf:Glass frit(6)BC:butyl carbitol,(7)BCA:butyl carbitol acetate

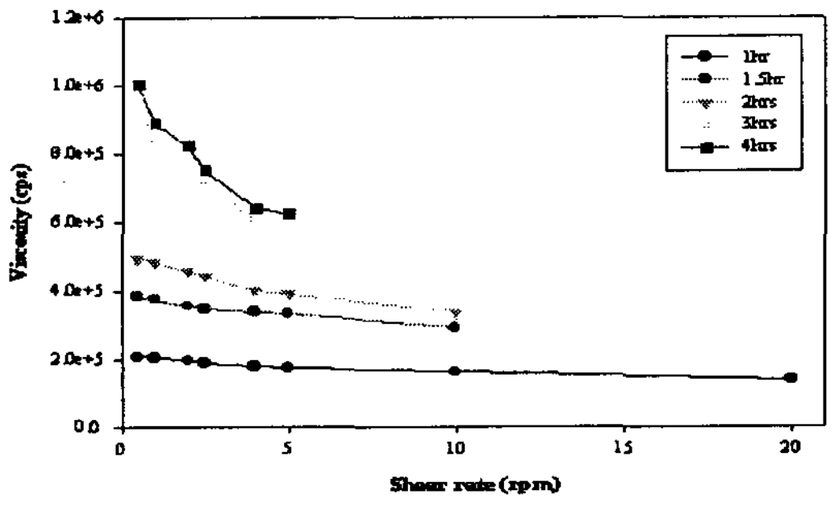


Fig. 2 Viscosity of Ag paste with 3-roll mixing time

3.2 Binder Polymer Mixture vs. Screen Printing

Screen printing is one of most important processes in the photolithographic patterning of electrodes for PDP. As shown in Table 3 and Fig.3 the screen printing property is dependent on the kind and amonnt of binder polymers. Mixture of cellulose and acrylate binder polymer resulted in reduced foam formation during screen printing due to hydrophilic-lypophilic balance

Table 3. Photosensitive Ag Paste Formulation vs. Screen Printing

No	BP (g)	Sol (g)	HPC (g)	3M MB (g)	PM (g)	PI (g)	Ag (g)	Gf (g)
ACP-13	5	4.5	-	-	2.5	0.4	22.3	0.73
ACP-14	5	4.5	-	-	2.5	0.4	21.88	1.15
ACP-15	5	4.5	-	-	2.5	0.4	21.4	1.63
ACP-16	5	6.5	0.5	2	8.25	0.66	40.4	2.13
ACP-17	5	6.5	1.0	4.0	9.0	0.72	46.3	2.43
ACP-18	5	6.5	1.5	6.0	9.75	0.78	52.1	2.74

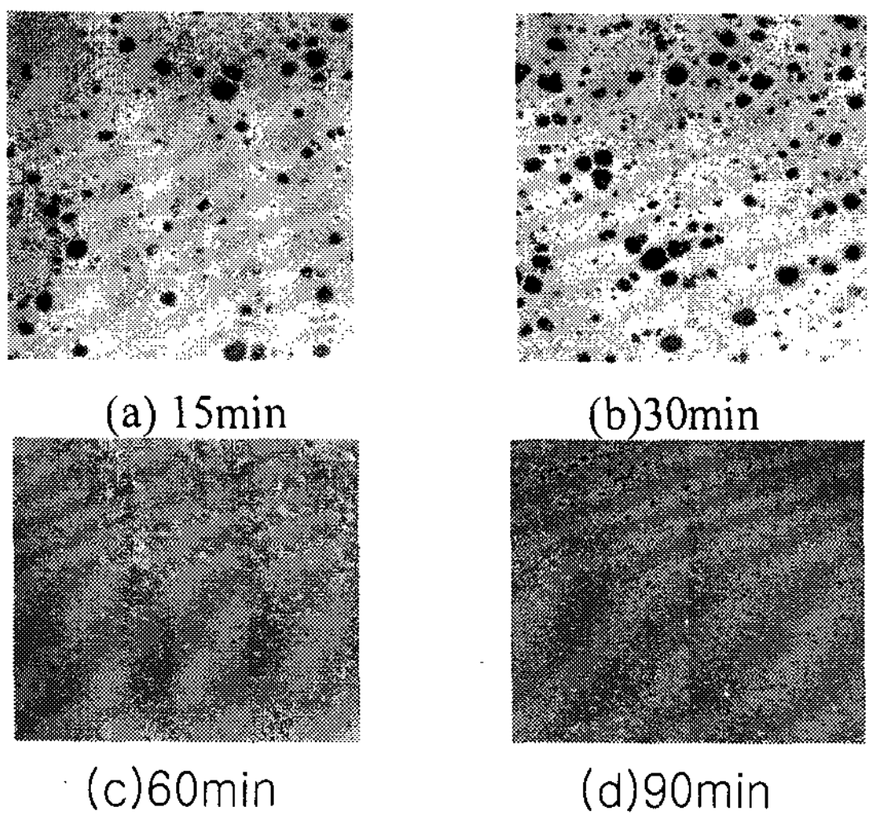


Fig.3. Photomicroscope image of screen printied Ag paste

3.3 UV Exposure and Paste Formulation

After selecting the proper binder polymer and solvent system, the amount of photocrosslinkable monomer and photoinitiator was determined. As shown in Table 4 and Fig.4, the necessary amount of multifunctional monomer was found to be at about 150% of the binder polymer to give good pattern property. The photoinitiator was needed at about 12% of binder polymer to give a sharp patterning of silver electrode. When photoinitiator was above this level some part of the electrode pattern was either undeveloped or some small islands of undeveloped layer remained along the silver electorde line pattern.

Talbe 4. Photosensitive Ag Paste vs. UV Exposure

No	BP (g)	TX (g)	HPC (g)	3M MB (g)	PM (g)	PI (g)	Ag (g)	Gf (g)
ACP-20	5	6.5	1.75	7	3.38	1.0	43.4	2.3
ACP-21	5	6.5	1.75	7	6.75	1.0	49.4	2.6
ACP-22	5	6.5	1.75	7	10.1	1.0	55.4	2.9
ACP-23	5	6.5	1.75	7	10.1	0.8	55	2.9

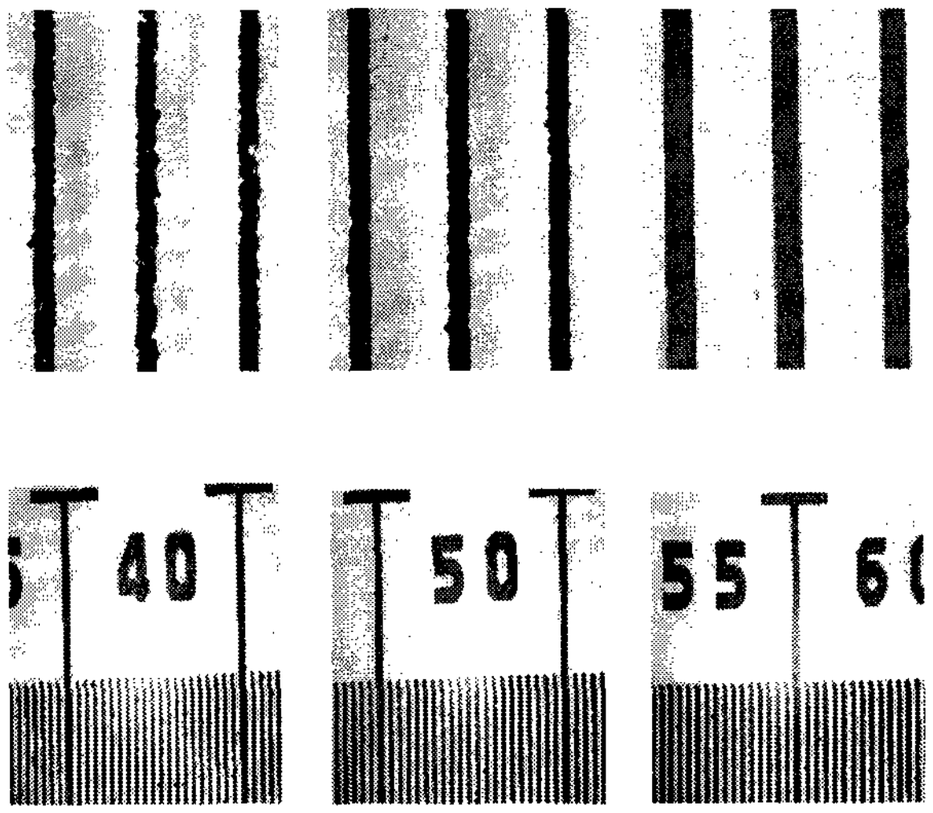
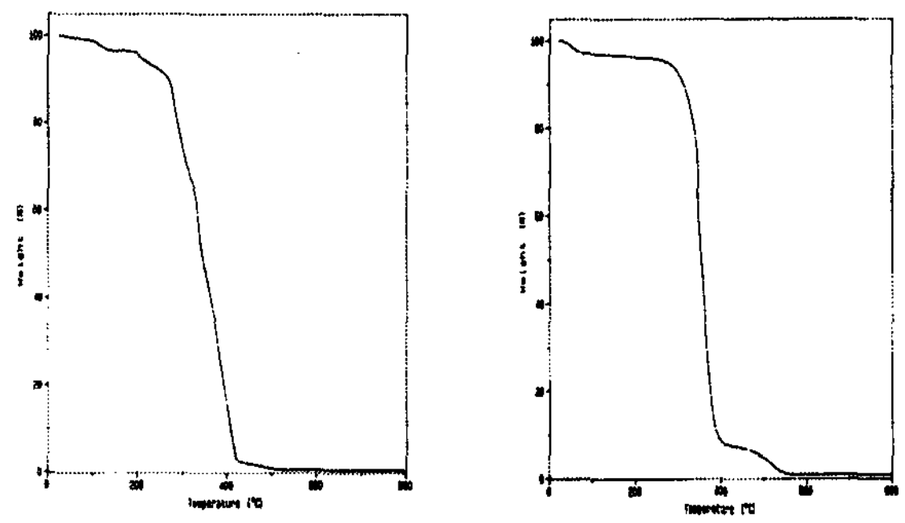


Fig.4 Ag Electrode Pattern vs. Formulation

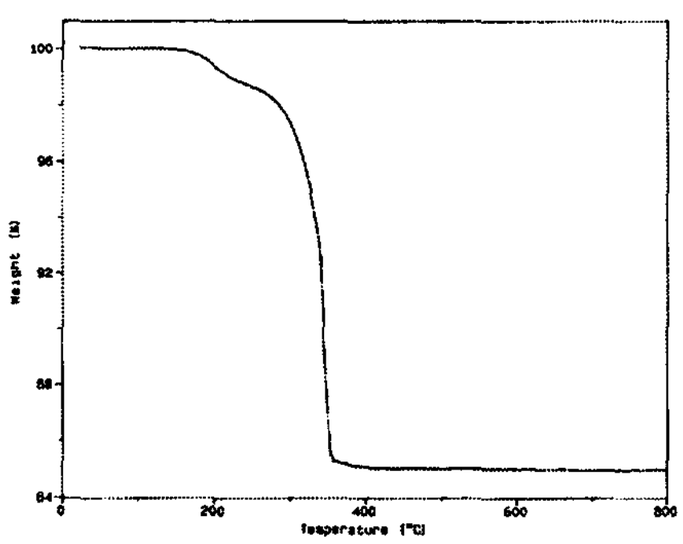
From Fig.4 it is noted that the proper selection of the binder polymer /solvent mixture system and optimum formulation could give resolution of Ag electrode up to 40 ㎛ when the UV exposure time and development condition were controlled.

3.4 Sintering vs. Ag Electrode Pattern.

The use of combination of cellulose and acrylate type binder polymer also had advantage in the sintering of electrode pattern. As shown in Fig.5, the acrylate polymer alone gave higher thermal decomposition temperature compared to the cellulose(HPC) type binder polymer. It was noted that the combined system exhibited very similar thermal decomposition behavior to that of cellulose binder polymer. The high initial decomposition rate of cellulose binder polymer could control edge curl formation to a minimum extent as shown in Fig.6.

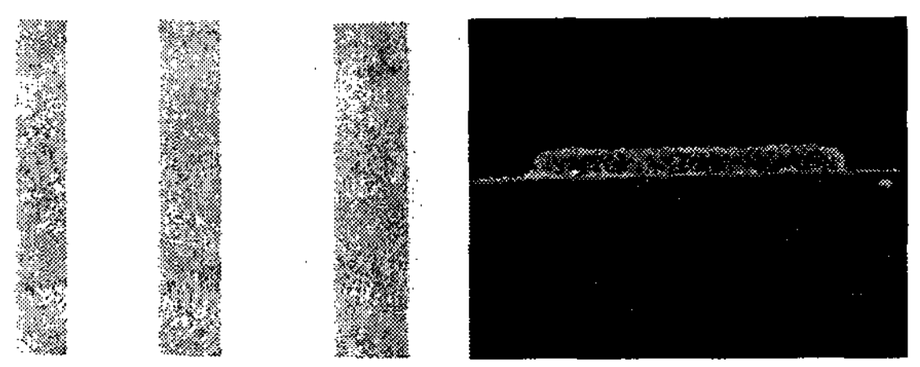


(a) MMA/MAA copolymer (b)HPC



(c)After exposure

Fig.5. TGA thermograms of binder polymer



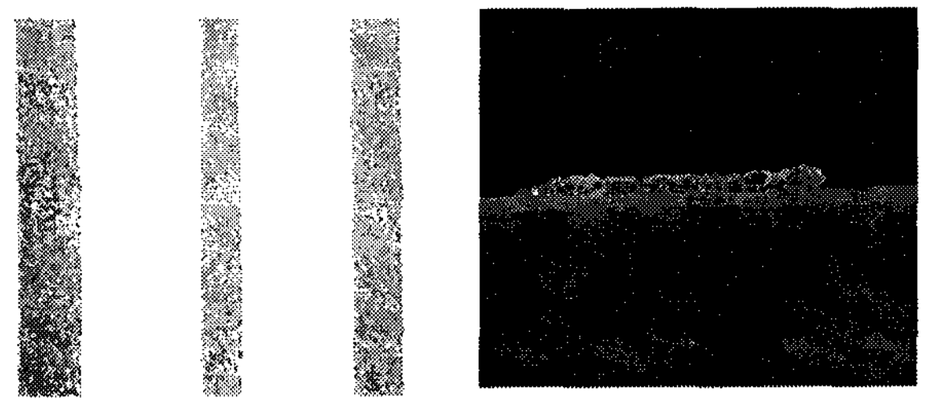


Fig.6. Ag electrode pattern after sintering process

4.Conclusion

It was found that the selection and relative amount of each component of photosensitive elecrode paste had effect on the photolithographic process of electrode patterning for PDP. The combination of cellulose(HPC) and acrylate (Poly(MMA-co-MAA) type binder polymer resulted in especially useful property both in the screen printing, development and sintering process of the photosensitive electrode paste.

5.Reference

1. 出水　可, “最新　プラス　マディスプレイ製造技術”, Press Journal, p.252-254(1997)
2. Arnost Reiser, Photoreactive polymers ; The science and technology of resists, A wiley-interscience publication, New York (1989)
3. Christian Decker, “Radiation Curing in Polymer Science and Technology,” Vol.Ⅲ: Poymerization Mechanism p. 33 (1993)
4. “Flat Panel Display”, PDP Technology, p202(1997)
5. “Technology and Materials of Color Plasma Display Panel”, Shiomusi, p 88(1996)
6. Lorenz.H.,et al.,,Sens.Act.A,64(1),33(1998)