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A study on the application of UV curing ink with sulfonate type acid amplifier

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Abstract−In this paper, both mono-type: 4-hydroxycyclohexyl-4-vinylbenzenesulfonate(CHDv-m), 4-(4-hydroxycyclohexyl) cyclohexyl-4-vinylbenzenesulfonate(BCDv-m), 4-(2-(4-hydroxycyclohexyl)propan-2-yl)-cyclohexyl-4-vinylbenzenesulfonate(IPDHv-m), 4-hydroxycyclohexyl-4-methylbenzenesulfonate(CHDp-m), 4-(4-hydroxycyclohexyl)-cyclohexyl-4-methylbenzenesulfonate(BCDp-m) and 4-(2-(4-hydroxycyclohexyl)propan-2-yl)-cyclohexyl-4-methylbenzenesulfonate(IPDHp-m) and di-type: 4,4′-di(vinylbenzenesulfonatyl)-cyclohexane(CHDv-d), 4,4′-di(vinylbenzenesulfonatyl)-1,1′-bicyclohexane(BCDv-d), 4,4′-di(vinlylbenzenesulfonatyl)-isopropylidene-dicyclohexane(IPDHv-d), 1,4-ditosyloxy cyclohexane(CHDp-d), 4,4′-ditosyloxy-1,1′-bicyclohexane(BCDp-d) and 4,4′-ditosyloxy isopropylidene dicyclohexane (IPDHp-d) acid amplifiers were synthesized. Their properties were characterized by ^{1}HNMR and DSC measurements. UV curing properties of samples prepared by using novel acid amplifiers were examined by measuring the change of current according to UV radiation time and intensity. Also, the application of acid amplifiers to UV inks was suggested. It was found that UV vehicles and inks with acid amplifier of 4-4′di(vinylbenzenesulfonatyl)-cyclohexane(CHDv-d) had a more rapid degree of curing than other samples.

Key words: UV Ink, UV Curing Process, Acid Amplifier, Acid Amplification

INTRODUCTION

The technologies of printing inks cured by ultraviolet (UV) light have been applied in the printing industries and their demands are increasing rapidly. Especially, because of the problems of environmental pollution, the need for free-pollution inks is increasing. It is inevitable to use UV cured inks in order to reduce organic solvents because they'll solve the environmental and health problems generated by use of solvent-type inks.

Furthermore, UV cured inks are suitable for high-speed printing and applicable to thermally unstable materials. Besides, UV cured inks have shown that their durability against friction and chemicals is relatively higher than solvent-type inks and can be applied to various fields [Na et al., 2005; Lee et al., 2003; Chai et al., 2000; Jung et al., 1997; Kim et al., 1996; Han and Woo, 1993].

Generally, the UV curing process is divided into radical mechanism and ion mechanism. Radical mechanism is that the photo-initiator is radicalized by UV irradiation and then both monomer and prepolymer are polymerized with the photo-initiator. On the other hand, for the ion mechanism the photo acid is generated by UV irradiation from the cation photo-initiator and then monomer is cured. At this time, the photo acid generated is produced linearly. Also, in the previous literature [Sada et al., 1995, 1996; Lee et al., 2003; McKean et al., 1989, 1991], the photo acid is noted to act on the system as a catalyst. Therefore, it improves both degree of cure and curing velocity.

In order to find applications of ion curing-type acid amplifiers to the UV ink process, the following tests and measurements are taken:

(1) Synthesis of intermediate to synthesize acid amplifiers.
(2) Synthesis of mono-type and di-type acid amplifiers.
(3) Design of equipment to measure the current according to UV curing process.
(4) Measurement of the change of current according to UV irradiation time and intensity.
(5) Investigation of the degree of cure, curing rate and its sensitivity according to UV irradiation time.
(6) Analysis of efficacies and effects for acid amplifiers.

EXPERIMENTAL

1. Synthesis of Acid Amplifiers

1-1. Reagent

In this experiment, 1,4-cyclohexanediol (CHD), 4,4'-bicyclohexyldiol (BCD), 4,4'-isopropylidene dicyclohexanol (IPDH) (Aldrich Chem. Co., 95.0%), 4-stylenesulfonicacid sodium salt hydrate, p-toluenesulfonyl chloride (pTSC, Aldrich Chem. Co., 98%) and thionyl chloride (Fluka. 98.0%) were used without further purification. Solvents were pyridine and dimethylformamide (DMF, Junsei Chem. Co).

1-2. Synthesis Of Intermediate(4-vinylbenzene-1-sulfonyl Chloride)

Under nitrogen, thionyl chloride (1 mole, 120 g) was added to a suspension of 4-styrenesulfonic acid sodium salt hydrate (0.2 mole, 41.24 g) in DMF (150 mL) at 0 °C with stirring. The resulting solution was stirred at 0 °C for 24 hr and then the mixture was allowed to warm to room temperature. Water was added to quench the reactor, and organic layer was extracted with dichloromethane and washed with 5 wt% aqueous solution of HCl and water repeatedly. The mixture was dried with $MgSO_4$ and the solvent was removed under reduced pressure to yield 4-vinylbenzene-1-sulfonyl chloride.

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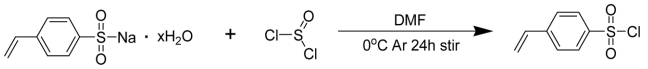


Fig. 1. Synthesis of 4-vinylbenzene-1-sulfonyl chloride (Intermediate).

[Yield: 50.1%, ^{1}HNMR ($CDCl_3$, ppm): 5.4931-5.5240 (d, 1H, J= 0.0309), 5.9185-5.9621 (d, 1H, J=0.0456), 6.7114-6.7826 (dd, 2H, J=0.0275), 7.5634-7.5843 (d, 2H, J=0.0209), 7.9364-7.9579 (d, 2H, J=0.0215)]

1-3. Synthesis of Mono-type Acid Amplifiers (CHDv-m, BCDv-m, IPDHv-m)

Intermediate (4-vinylbenzne-1-sulfonyl chloride, 0.04 mole, 8.2 g) was added to a suspension of CHD (0.04 mole, 4.65 g) in pyridine (150 mL) at 0 °C with stiring. The resulting solution was stirred for 24 hr. Water was added to quench the reactor, and organic layer was extracted with chloroform ($CHCl_3$) and washed repeatedly with 5 wt% aqueous soloution of HCl and water. The mixture was dried with $MgSO_4$ and the solvent was removed under reduced pressure to yield 4-hydroxycyclohexyl-4-vinylbenzenesulfonate (CHDv-m).

[Yield: 48%, m.p: 120, ^{1}HNMR ($CDCl_3$, ppm): 1.6214-1.6954 (m, 4H), 1.8124-1.8632 (m, 4H), 3.0197 (m, 1H), 4.0100 (s, 1H), 4.7163 (m, 1H), 5.4323-5.4593 (d, 2H, J=0.0270), 5.8434-5.9074 (d, 2H, J=0.0440), 6.6932-6.7372 (dd, 1H, J=0.0274), 7.5113-7.4324 (d, 2H, J=0.0211), 7.8028-7.8234 (d, 2H, J=0.0206)]

By the same process, 4-(4-hydroxycyclohexyl)cyclohexyl-4-vinylbenzenesulfonate (BCDv-m) was yielded by synthesizing 4,4'-bicyclohexyldiol (BCD, 0.04 mole, 8.1 g) and intermediate(4-vinylbenzene-1-sulfonyl chloride, 0.04 mole, 8.2 g).

[Yield: 56%, m.p : 136, ^{1}HNMR ($CDCl_3$, ppm): 0.9060-0.9674 (m, 6H), 1.3588-1.4382 (m, 4H), 1.6534-1.6807 (m, 4H), 1.9214-1.9465 (m, 4H), 3.1240-3.2145 (m, 1H), 4.0128 (s, 1H), 4.3271-4.3359 (m, 1H), 5.4326-5.4600 (d, 1H, J=0.0274), 5.8691-5.9130 (d, 1H, J=0.0436), 6.6974-6.7414 (dd, 1H, J=0.0274), 7.5097-7.5312 (d, 2H, J=0.0225), 7.8177-7.8384 (d, 2H, J=0.0207)]

As the same process, 4-(2-(4-hydroxycyclohexyl)propan-2-yl)-cyclohexyl-4-vinylbenzenesulfonate (IPDHv-m) was yielded by synthesizing 4-4′-isopropylidene dicyclohexanol (IPDH, 0.04 mole, 9.62 g) and intermediate(4-vinylbenzene-1-sulfonyl chloride, 0.04 mole, 8.2 g).

[Yield: 52%, m.p : 138 ^{1}HNMR ($CDCl_3$, ppm): 0.6568-0.69521 (m, 6H), 0.9851-1.0604 (m, 4H), 1.1452-1.1720 (m, 2H), 1.3274-1.4374 (m, 4H), 1.6327-1.6512 (m, 4H), 1.9543-1.9987 (m, 4H), 3.1332-3.2100 (m, 1H), 4.001 (s, 1H), 4.3211-4.3641 (m, 1H), 5.4320-5.4594 (d, 2H, J=0.0274), 5.8689-5.9129 (d, 2H, J=0.0440), 6.7050-6.7490 (dd, 1H, J=0.0274), 7.5155-7.5362 (d, 2H, J=0.0207), 7.8276-7.8483 (d, 2H, J=0.0207)]

1-4. Synthesis of Mono-type Acid Amplifiers (CHDp-m, BCDp-m, IPDHp-m)

p-toluenesulfonyl chloride (pTSC, 0.04 mole, 7.62 g) was added to a suspension instead of the intermediate. As the same process, 4-hydroxycyclohexyl-4-methylbenzenesulfonate (CHDp-m) was yielded.

[Yield: 50.1%, m.p: 134, ^{1}HNMR ($CDCl_3$, ppm): 1.50-1.53 (m, 4H), 1.77-1.92 (m, 4H), 2.32 (s, 6H), 3.55-3.56 (m, 1H), 4.37-4.47 (m, 1H), 7.22 (d, 4H, J=0.0207), 7.65 (d, 4H, J=0.0206)]

As the same process, 4-(4-hydroxycyclohexyl)-cyclohexyl-4-methylbenzenesulfonate (BCDp-m) was yielded by synthesizing 4,4'-bicyclohexyldiol (BCD, 0.04 mole, 8.1 g) and p-toluenesulfonyl chloride (pTSC, 0.04 mole, 7.62 g).

[Yield: 57.5%, m.p: 149, ^{1}HNMR ($CDCl_3$, ppm): 0.95-1.18 (m, 10H), 1.70-1.72 (m, 8H), 2.42 (s, 3H), 3.46-3.50 (m, 1H), 4.30-4.34 (m, 1H), 7.29 (d, 2H, J=0.0207), 7.75 (d, 2H, J=0.0207)]

As the same process, 4-(2-(4-hydroxycyclohexyl)propan-2-yl)-cyclohexyl-4-methylbenzenesulfonate (IPDHp-m) was yielded by synthesizing 4,4'-isoproylidene dicyclohexanol (IPDH, 0.04 mole, 9.62 g) and p-toluenesulfonyl chloride (pTSC, 0.04 mole, 7.62 g).

[Yield: 43.8%, m.p: 175, ^{1}HNMR ($CDCl_3$, ppm): 1.013-1.04 (m, 8H), 1.18-1.21 (m, 5H), 1.22-1.43 (m, 7H), 1.68 (d, 2H, J=0.0257), 1.98 (d, 2H, J=0.0257), 2.43 (s, 3H), 3.49-3.51 (m, 1H), 4.02 (s, 1H), 4.07-4.39 (m, 1H), 7.30 (d, 2H, J=0.0207), 7.76 (d, 2H, J= 0.0206)]

1-5. Synthesis of Di-type Acid Amplifiers (CHDv-d, BCDv-d, IPDHv-d)

By the same process, 4-4'-di(vinylbenzenesulfonatyl)-cyclohexane (CHDv-d) was yielded by synthesizing 1,4-cyclohexanediol (CHD, 0.04 mole, 4.65 g) and intermediate (4-vinylbenzene-1-sulfonyl chloride, 0.08 mole, 16.4 g).

[Yield: 45.0%, m.p: 126, ^{1}HNMR ($CDCl_3$, ppm): 1.6186-1.6474 (m, 4H), 1.8422-1.8656 (m, 4H), 4.6163 (m, 2H), 5.4452-5.4726 (d, 2H, J=0.0274), 5.8741-5.9176 (d, 2H, J=0.0435), 6.7048-6.7488 (dd, 2H, J=0.0440), 7.5198-7.409 (d, 4H, J=0.0211), 7.8107-7.8318 (d, 4H, J=0.0211)]

4,4'-di(vinylbenzenesulfonatyl)-1,1'-bicyclohexane (BCDv-d) was yielded by synthesizing 4,4'-bicyclohexyldiol (BCD, 0.04 mole, 8.1 g) and intermediate (4-vinylbenzene-1-sulfonyl chloride 0.08 mole,

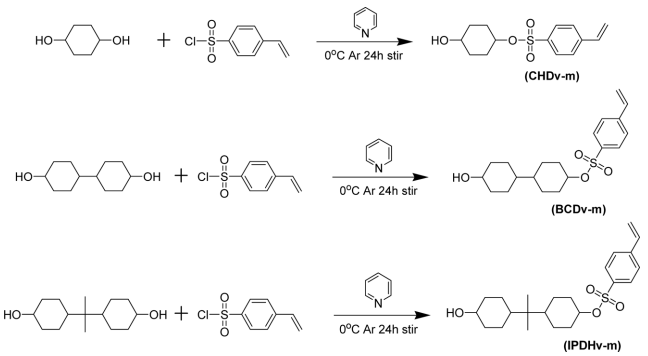


Fig. 2. Mono-type acid amplifiers.

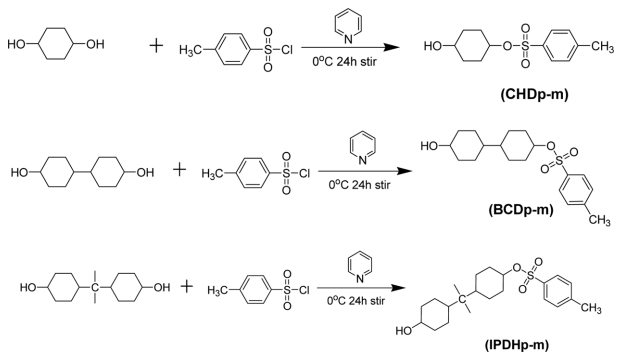


Fig. 3. Mono-type acid amplifiers.

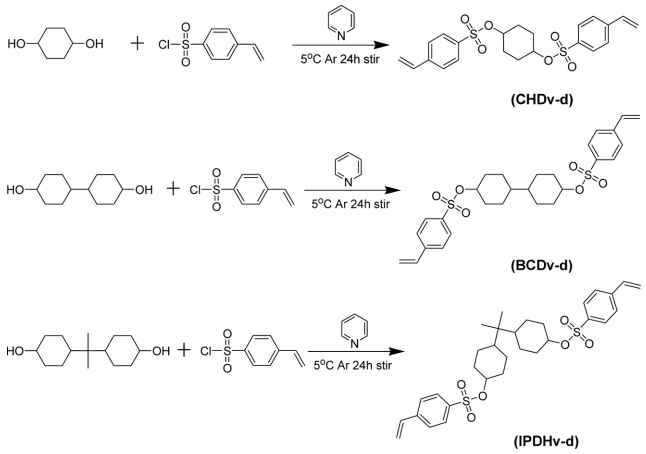


Fig. 4. Di-type acid amplifiers.

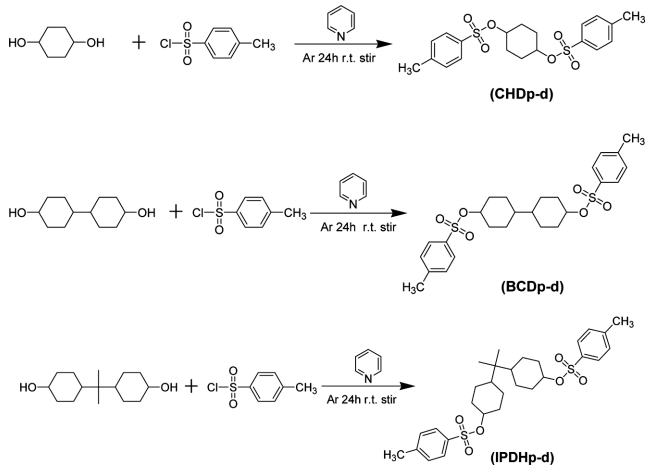


Fig. 5. Di-type acid amplifiers.

16.4 g). [Yield: 4 3.0%, m.p: 205, ^{1}HNMR ($CDCl_3$, ppm): 0.9076-0.9574 (m, 6H), 1.3597-1.4482 (m, 4H), 1.6534-1.6808 (m, 4H), 1.9215-1.9454 (m, 4H), 4.3280-4.3409 (m, 2H), 5.4329-5.4603 (d, 2H, J=0.0274), 5.8695-5.9134 (d, 2H, J=0.0436), 6.7046-6.7486 (dd, 2H, J=0.0269), 7.5146-7.5357 (d, 4H, J=0.0211), 7.8234-7.8442 (d, 4H, J=0.0211)]

4,4'-di(vinylbenzenesulfonatyl)-isopropylidene-dicyclohexane (IPDHv-d) was yielded by synthesizing 4-4'-isopropylidene dicyclohexanol (IPDH, 0.04 mole, 9.62 g) and intermediate (4-vinybenzene-1-sulfony-l chloride, 0.08 mole, 16.4 g).

[Yield: 49.5%, m.p: 141, ^{1}HNMR ($CDCl_3$, ppm): 0.6225-0.6836 (m, 6H), 0.9494-1.0096 (m, 4H), 1.0940-1.1533 (m, 2H), 1.3365-1.4285 (m, 4H), 1.6153-1.6472 (m, 4H), 1.9463-1.9683 (m, 4H), 4.3181-4.3414 (m, 2H), 5.4339-5.4613 (d, 2H, J=0.0274), 5.8713-5.9153 (d, 2H, J=0.0440), 6.7060-6.7770 (dd, 2H, J=0.0440, 0.0274), 7.5170-7.5381 (d, 4H, J=0.0211), 7.8286-7.8493 (d, 4H, J=0.0207)]

1-6. Synthesis of Di-type Acid Amplifiers (CHDp-d, BCDp-d, IPDHp-d)

1,4-ditosyloxyl cyclohexane (CHDp-d) was yielded by synthesizing 1,4-cyclohexanediol (CHD, 0.04 mole, 4.65 g) and p-toluenesulfonyl chloride (pTSC 0.08 mole 15.24 g).

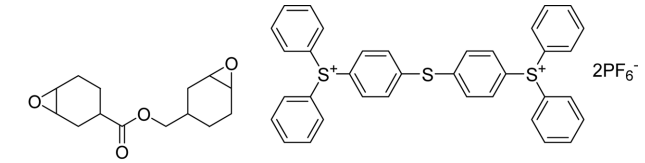
[Yield: 40.0%, m.p: 158, ^{1}HNMR ($CDCl_3$, ppm): 1.5962-1.6347 (m, 4H), 1.8304-1.8570 (m, 4H), 2.4405 (s, 6H), 4.5908 (m, 2H), 7.3132-7.3346 (d, 4H, J=0.0214), 7.7479-7.7689 (d, 4H, J=0.0210)]

4,4'-ditosyloxy-1,1'-bicyclohexane (BCDp-d) was yielded by synthesizing 4,4'-bicyclohexane (BCD, 0.04 mole, 8.1 g) and p-toluenesulfonyl chlorie (pTSC, 0.08 mole, 15.24 g).

[Yield: 44.3%, m.p: 143, ^{1}HNMR ($CDCl_3$, ppm): 0.9367-0.9551 (m, 6H), 1.3481-1.4072 (m, 4H), 1.6394-1.6775 (m, 4H), 1.9110-1.9352 (m, 4H), 2.4246 (s, 6H), 4.2987-4.3213 (m, 2H), 7.2977-7.3183 (d, 4H, J=0.0207), 7.7514-7.7721 (d, 4H, J=0.0207)]

4,4'-ditosyloxy isopropylydene dicyclohexane (IPDHp-d) was yielded by synthesizing 4-4'-isopropylidene dicyclohexanol (IPDH, 0.04 mole, 9.62 g) and p-toluenesulfonyl chloride (pTSC, 0.08 mole, 15.24 g).

[Yield: 41.0%, m.p: 144, ^{1}HNMR ($CDCl_3$, ppm): 0.6300-0.6915 (m, 6H), 0.9523-1.0118 (m, 4H), 1.1277-1.2659 (m, 2H), 1.3616-1.3893 (m, 4H), 1.6172-1.6490 (m, 4H), 1.9443-1.9665 (m, 4H), 2.4330 (s, 6H), 4.3070-4.3296 (m, 2H), 7.3052-7.3251 (d, 4H, J=0.0199), 7.7633-7.7844 (d, 4H, J=0.0207)]



3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate [UVR-6100]

Bis [(4-diphenylsulphonio)-phenyl] sulphide bis-hexafluorophosphate [UVI-6900]

Fig. 6. Structures of compounds used in this paper.

Table 1. The product name and CAS No. of pigment

	Product name	CAS No.
Cyan	Panax blue BS-7000	147-14-8
Magenta	Panax Carmine HF-S03	5281-04-9
Yellow	Panax Yellow 2GL	5468-75-7

2. Sample and Measurement System

2-1. Formulation of Samples

Monomer was an ion curing-type (3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (UVR-6100, Aldrich Chem. Co., 98.0%) and photo-initiator was bis[(4-diphenylsulphonio)-phenyl] sulphide bis-hexafluorophosphate (UVI 6900, Union Carbide). Their structures are shown in Fig. 6.

Pigments (Ukseung Chemical) used in this paper are represented in Table 1. And samples are described in Table 2.

The absorption characteristics of samples are shown by UV/vis spectroscopy (SHIMADZU. UV-2101PC) (Fig. 7). From Fig. 7, in each monomer and acid amplifier or in a compound type, the absorptions of photo were not generated. Thus, in this case, they were not concerned with UV curing reaction directly.

In order to find the current of samples, by using a vacuum plating system, slide glass, indium, platinum wire and aluminum electrodes, the sample cell was designed as in Fig. 8.

2-2. Measurement System

To measure the current of samples, the measuring system was composed of a UV lamp (light source, xenon lamp; power, 500W; wavelength range, more than 300 nm; type, UXL-500D-O, UshioDenki, Tokyo, Japan), Electrometer (M.617, Keithley Co.), GPIB

Table 2. The ratio of monomer, PI, AA(CHDv-m,CHDv-d) and pigment

Sample	Monomer	PI	Acid amplifier		Cyan	Magenta	Yellow
			CHDv-m	CHDv-d			
SM-1	1 g	×	×	×	×	×	×
SM-2	×	0.03 g	×	×	×	×	×
SM-3	1 g	×	0.03 g	×	×	×	×
SM-4	1 g	0.03 g	×	×	×	×	×
SM-5	1 g	0.03 g	0.03 g	×	×	×	×
SM-6	1 g	0.03 g	×	0.03 g	×	×	×
SM-7	1 g	0.03 g	×	×	0.03 g	×	×
SM-8	1 g	0.03 g	×	×	×	0.03 g	×
SM-9	1 g	0.03 g	×	×	×	×	0.03 g
SM-10	1 g	0.03 g	0.03 g	×	0.03 g	×	×
SM-11	1 g	0.03 g	0.03 g	×	×	0.03 g	×
SM-12	1 g	0.03 g	0.03 g	×	×	×	0.03 g
SM-13	1 g	0.03 g	×	0.03 g	0.03 g	×	×
SM-14	1 g	0.03 g	×	0.03 g	×	0.03 g	×
SM-15	1 g	0.03 g	×	0.03 g	×	×	0.03 g

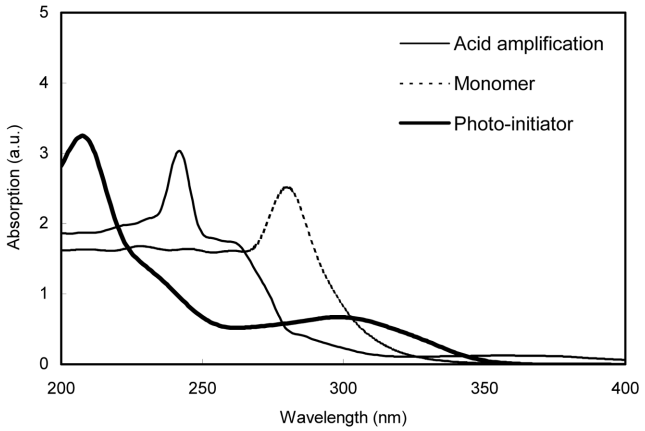


Fig. 7. Absorption spectrum of compounds applied in this paper.

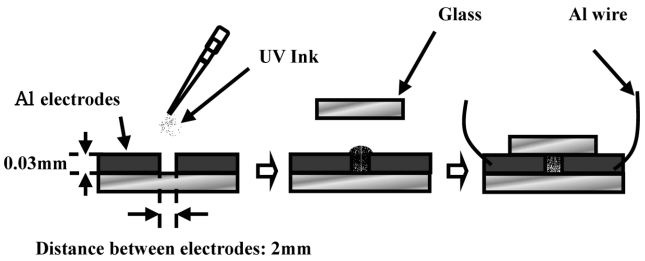


Fig. 8. Manufacture of sample cell.

interfaces card (NI Co.) and PC (IBM Co.). With Labview (6.1 Program, NI Co.) a direct-measuring program was designed and the circuit was controlled. Between the light source and the samples, an L-type adapter was connected. The radiation intensity was measured by IL390C Light Bug (International Light Co.).

RESULTS AND DISCUSSION

1. Consideration of Vehicle's Curing Properties

3-1. The Change of Current According to UV Irradiation Time

Using the previous studies (Fig. 10) of Y. Takahashi [Tada et al., 1995, 1996; Takahashi et al.] that examined the UV ink's electronic properties, in this study, the UV curing properties of the samples and the change of current of samples involving the synthesized acid amplifiers were represented and also the pigmented system was investigated.

A current of about 15 μA flowed after impressing voltage and then the current was rapidly reduced on UV irradiation. The magnitude of the current was reduced below half of the initial current after 90 sec and reduced below 5 μA after 180 sec.

3-1-1. The Change of Current for Sample Added Acid Amplifier

Into the samples, which consisted of photopolymerization monomer, photoinitiator and acid amplifier (main-chain was CHD [1,4-cyclohexanediol]), UV was irradiated for 180 sec. And then the change of current was measured (Fig. 11).

The initial current for the samples (SM-4, 5, 6, 32, 33) was similar after UV irradiation but the change of current had a remarkable difference in proportion to UV irradiation time. After 30 sec, the change of current followed in the order as CHDp-m>CHDp-d>CHDv-m >CHDv-d. And the current of sample added CHDv-d was third of samples with no acid amplifier. It was the reason that at the double-bond of the vinyl group radical polymerization was promoted more, and more than at a methyl group and di-type increased the generation of acid more than mono-type.

3-2. The Quantity of Current Change According to UV Intensity

In order to examine the quantity of current change, as shown in Eq. (1), UV was irradiated during 10 sec and then the results were plotted (Fig. 12). Also, the relations to vehicles and pigmented samples are represented in Fig. 13.

$$\Delta I = k \cdot \Phi \quad (1)$$

(where, 'ΔI' is the quantity of current changing, 'k' is a constant and 'Φ' is UV intensity.)

The curves representing the relation between UV intensity and

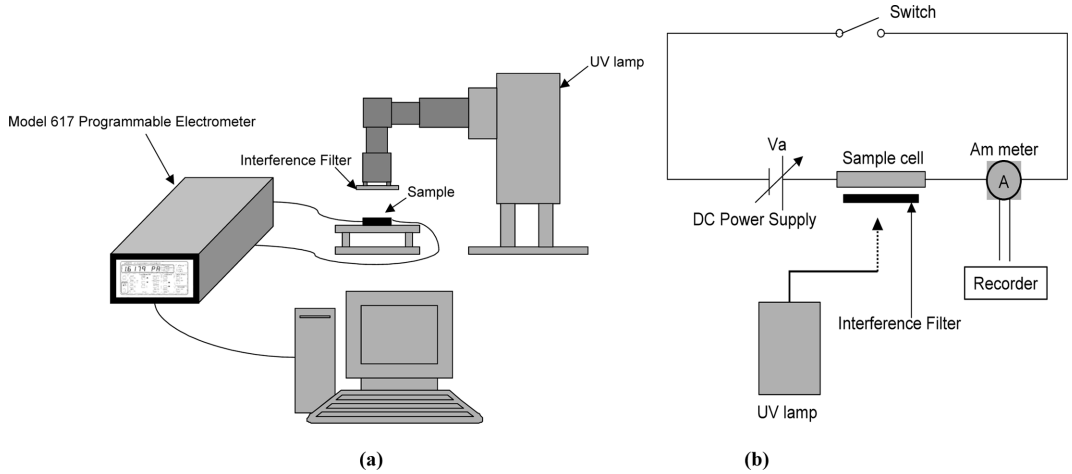


Fig. 9. Apparatus for measurement of conduction current in UV curable layer.

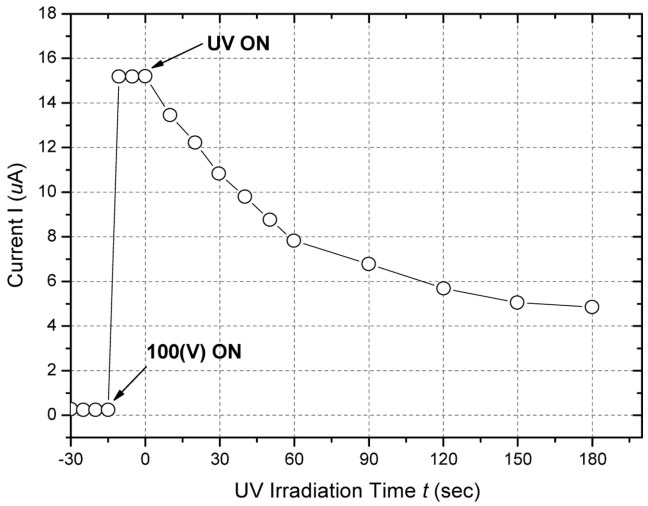


Fig. 10. Current change with UV irradiation time.

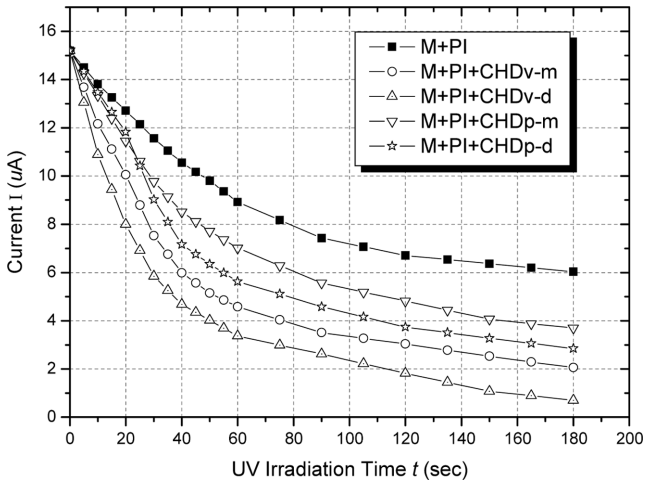


Fig. 11. Current change with UV irradiation time (SM-4, 5, 6, 32, 33).

quantity of current change according to acid amplifiers were nearly similar. At low range of UV intensity, the quantity of current change

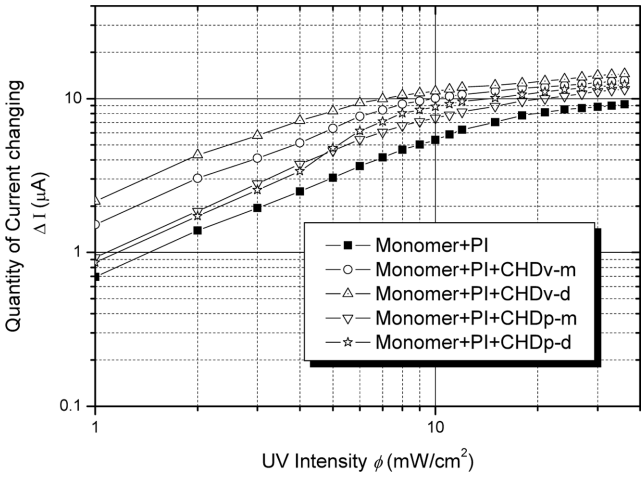


Fig. 12. The logarithmic plots for sample quantity of current change with UV intensity (SM-4, 5, 6, 32, 33).

(ΔI) was high in the vehicles with added acid amplifiers and increased with increasing UV intensity. It was concerned that vehicle's curing process was promoted because in the presence of acid amplifiers the generation of photo acids was amplified under low UV intensity.

Also, it implied that control of the degree of cure was possible by selection of acid amplifiers.

When pigment was added to the samples but not acid amplifiers, the quantity of current change for pigmented samples was lower than that of the samples which contained the pigment. It was shown that the quantity of current change of the samples with added acid amplifiers was increased again. By and large, the slopes of the quantity graphs of current change among each acid amplifier were similar in the case of vehicles but not in the case of pigmented samples.

3-3. Degree of Cure and Curing Rate According to UV Irradiation Time

By means of Eqs. (2) and (3), the degree of cure and curing rate was measured according to UV irradiation time.

$$R(\text{degree of cure}) = (I_0 - I_t)/I_t \times 100 = \Delta I/I_t \times 100\ (\%) \quad (2)$$

$$V(\text{curing rate}) = R/t\ (\%/\text{sec}) \quad (3)$$

Where 'R' is the degree of cure, 'I_0' the initial current, 'I_t' the current

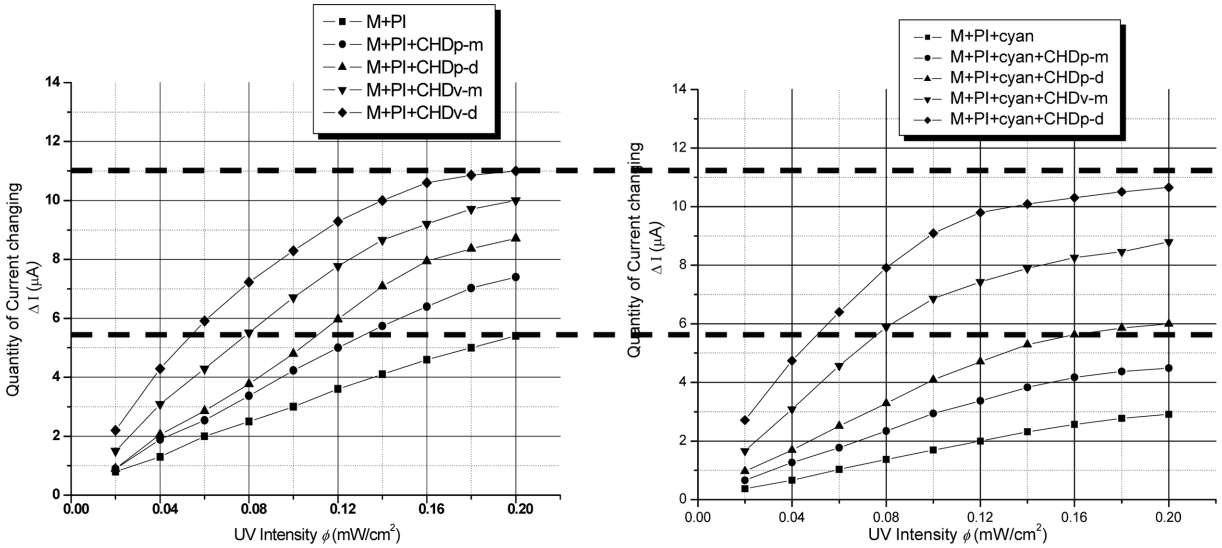


Fig. 13. The comparison of quantity of current change as a change of UV intensity between UV vehicle (CHD) and inks (cyan).

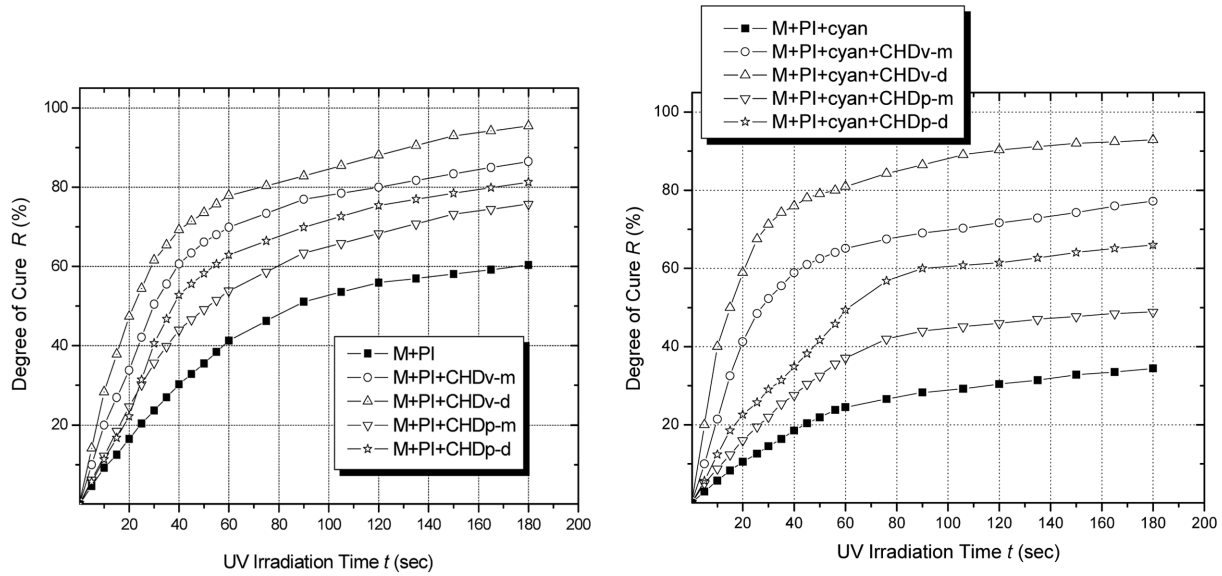


Fig. 14. The comparison of the degree of cure according to UV irradiation time between UV vehicles (CHD) and inks (cyan).

at time 't', 'ΔI' the quantity of current change, 'v' the curing rate, and 't' the time.

In Fig. 14(a), when the pigment was not added to the sample, the degree of cure was represented according to UV irradiation time. It was found that the degree of cure was about 60% after UV irradiation time of 180 sec. In Fig. 14(b), the degree of cure of cyan pigmented samples is shown and diminished about 35%. It was considered that UV light did not transmit to the inside of inks due to the pigment, and then reflected; thus the degree of cure was decreased. However, it was shown that the degree of cure was increased up to three times (90%) when the acid amplifiers were added.

Fig. 15(a) is the log-log plots of the curing rate versus UV irradiation time for the samples that did not pigment. On the other hand, Fig. 15(b) is for the pigmented samples. The curing rate was slow in the case of pigmented samples but was fast with the addition of acid amplifiers to the samples.

3-4. Comparison of the Curing Sensitivity for Acid Amplifiers According to UV Inks

From the following Eq. (4), the curing sensitivity was obtained for acid amplifiers.

$$S_i = R_{t=10}/(t \cdot \Delta) \ (\%/\text{sec} \cdot \text{mW/cm}^2) \quad (4)$$

where 'S_i' is the curing sensitivity, '$R_{t=10}$' the curing rate at 10 sec, 't' the time, and 'Φ' the UV intensity.

For all inks which did not have added the acid amplifiers, the curing sensitivity was low on the whole. CHDv-d had high curing sensitivity in cyan and magenta inks and BCDv-d had high curing sensitivity in yellow inks.

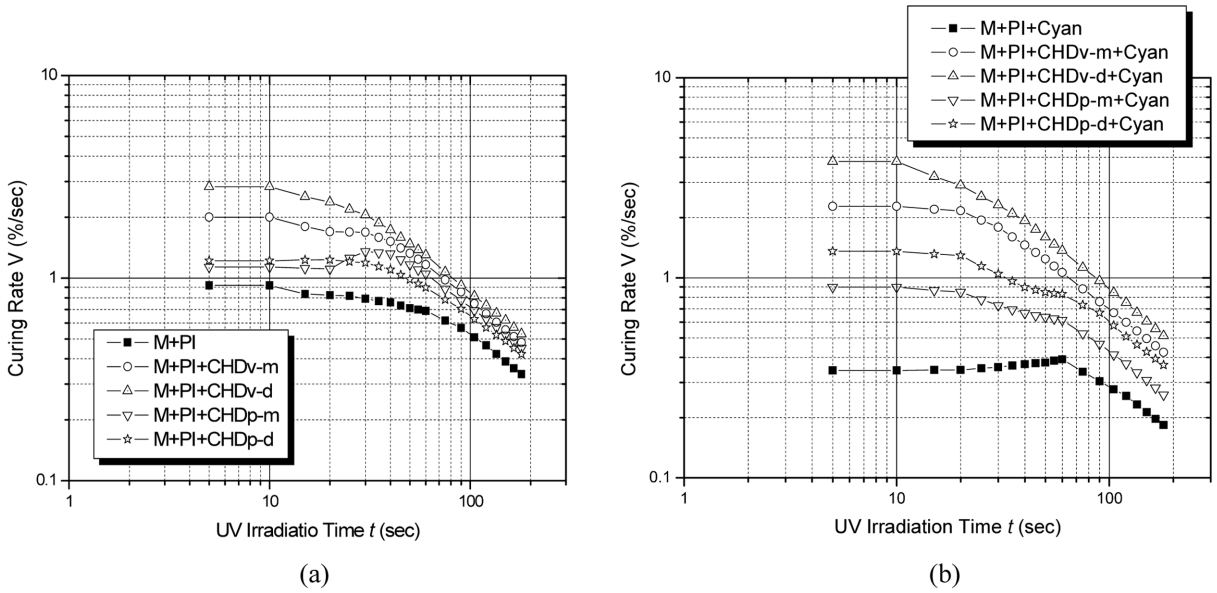


Fig. 15. A comparison of the curing rate according to UV irradiation time between UV vehicles (CHD) and inks (cyan).

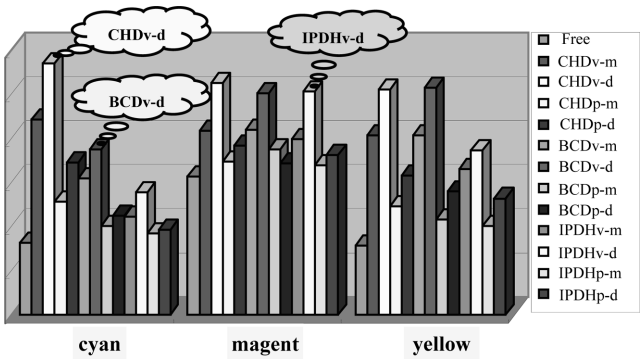


Fig. 16. The comparison of curing sensitivity.

CONCLUSION

1. The conventional UV curing measurement system was raised some problems such as the difficulties of handling, the limit of time, place and measurement range. Despite those problems, it was possible to simply measure UV curing properties by UV curing measurement system designed in this paper. It was handled conveniently on a PC.

2. It was shown that the photo-initiator was an important factor according to the results of electrical properties of UV vehicles and inks.

3. It was shown that the degree of cure and curing rate of UV vehicles and inks was increased by the addition of the acid amplifiers.

4. The acid amplifiers improved the UV curing rate in the following order: CHD>BCD>IPDH (according to diol compounds), vinyl>methyl (according to substitution), di-type>mono-type (according to the number of sulfoxide).

5. It was shown that the degree of cure and curing rate could be governed by the selection of acid amplifiers in a UV curing system.

NOMENCLATURE

ΔI : quantity of current change
k : constant
Φ : UV intensity
R : degree of cure
I_0 : initial current
V : curing rate
I_t : current at time t
t : irradation time
S_t : curing sensitivity
$R_{t=10}$: curing rate at 10 sec

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