CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

3.1.1 Green phosphor from NICHIA Chemical Industry Co., Ltd.

3.1.2 Poly(vinyl alcohol) from Nihon Gosei Chemical Industries Co., Ltd.

3.1.3 Ammonium dichromate ($(NH_4)_2Cr_2O_7$) from Kanto Kagaku Co., ltd.

3.1.4 Poly(oxypropylene glycol) solution

(Pluronic, $HO(C_2H_4O)_a(C_3H_6O)_b(OC_2H_4)_cOH$) from BASF Corporation.

3.1.5 Sodium polyacrylate solution (Tamol, $(C_2H_3COO^-)_nNa^+$) from Rohm & Hass Co., Ltd.

3.1.6 Sodium dodecyl sulfate solution (Alscoap, $CH_3(CH_2)_{11}OSO_3Na$) from Toho Chemical Industries Co., Ltd.

3.1.7 Acrylic emulsion (C-72, $(C_3H_4O_2)_n$) from Nihon Acrylic Chemical Co., Ltd.

3.1.8 Methanol (CH_4O) from Merck.

3.1.9 Potassium dihydrogen phosphate (KH_2PO_4) from Fluka.

3.1.10 Disodium hydrogen phosphate (Na_2HPO_4) from Fluka.

3.1.11 Citric acid monohydrate ($C_6H_8O_7.H_2O$) from Merck.

3.1.12 Sodium hydroxide (NaOH) from Carlo ERBA.

3.1.13 Sulfuric acid (H_2SO_4) from Merck.

3.1.14 Ammonia solution (NH_3 solution) from Reidel de Haen.

3.2 Instruments, machines and apparatus

3.2.1 Color XY analyzer

The color XY analyzer Model CA-100 from MINOLTA was used to measure the color value of screen in form of figures (X,Y) and screen corner brightness (CB).

3.2.2 pH meter

pH meter Model HM30V from TOA Electronics Ltd. was used for measuring the slurry pH during preparation.

3.2.3 Green coating machine

Green coating machine from TOSHIBA was used for green slurry coating. Normally it is for routine mass CDT production and also available for both Auto/ Manual dispensing.

3.2.4 Exposure machine

Exposure machine from TOSHIBA SEIKI was used to expose UV light to the coated panel. Normally it is for routine mass CDT production which its Exposure Quality (EQ), *i.e.* time, is adjustable.

3.2.5 Shop micrometer with UV light

Shop Micrometer from YASHIMA was used for dot size and quality check. It was used with UV light so that phosphor can be clearly seen to inspect.

3.2.6 ZAHN cup viscometer

ZAHN cup was used to measure the slurry viscosity in unit second.

3.2.7 Gravimeter

Gravimeter was used to measure the slurry specific gravity (SG).

3.2.8 Characteristic test set

The EIMAC characteristic test set model CHARACT-H1 from Toshiba was used for field light out put (FLO), screen color and brightness check.

3.3 Preparation of 8.5% PVA solution[a]

DI water (150 L) in a reactor tank with stirrer was heated and the temperature was controlled at 50°C. PVA (30 kg) was slowly filled into the reactor tank and stirred and another portion of DI water (75 L) was added. After 1 hour, the temperature inside was then raised to 70°C and 5% sodium dodecyl sulfate solution (600 mL) was added and stirred for 2 hours. Another portion of DI water (30 L) was added into the reactor tank. The temperature was then adjusted to 90°C, stirred for 3 hours and allowed to cool to room temperature. Solid content, pH value, viscosity and its appearance were finally inspected.

Note : [a] Refer to TDDT work instruction No. 14-06-008 (1997).

Table 3.1 Required inspection values of 8.5% PVA solution

Items	Required value
1. Solid content	8.3-8.7 %
2. pH (at 24 ± 2°C)	4.5-5.1
3. Viscosity (at 21±1°C)	1100 – 1400 cps
4. Appearance	Slightly opaque or transparent

3.4 Preparation of 10% ADC solution[a]

ADC (1000 g) in polyethylene bottle was dissolved in DI water (8.5 L) and ammonia water (0.55 L). The ADC solution was mixed by using milling machine over 1 hour. The ADC solution was then filtered and inspected for the specific gravity and pH value, respectively.

Table 3.2 Required specific gravity and pH of ADC solution

Items	Required value
1. Specific gravity	1.070-1.080 (at 24 ± 2°C)
2. pH value	7.3-7.5 (at 24 ± 2°C)

Note : [a] Refer to TDDT work instruction No. 14-06-011 (1999).

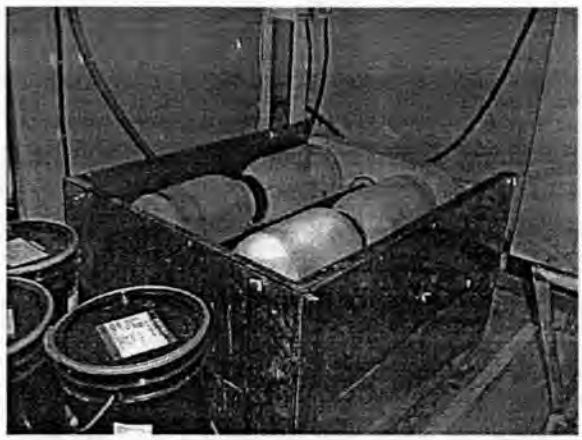

Figure 3.1 Milling machine for surfactant stocked solution preparation

3.5 Preparation of surfactant

3.5.1 Preparation of 5% poly(oxypropylene glycol) (pluronic) solution[a]

Pluronic solution (500 mL) was diluted in methanol (4,750 mL) and DI water (4,750 mL). The solution was mixed by milling machine for 30 minutes or more. The solution was then filtered before use.

3.5.2 Preparation of 5% sodium polyacrylate (tamol) solution[b]

Tamol solution (2,000 mL) was diluted in DI water (8,000 mL) in polyethylene bottle. The solution was mixed for 1 hour or more by milling machine.

Notes : [a] *Refer to TDDT work instruction No. 14-06-018 (2000).*
[b] *Refer to TDDT work instruction No. 14-06-012 (1999).*

3.5.3 Preparation of 5% dodecyl sulfate sodium salt (alscoap) solution[a]

Alscoap solution (500 mL) was diluted in DI water (95,000 mL) and mixed for 30 minutes or more by milling machine.

3.5.4 Preparation of 45% acrylic emulsion

Acrylic emulsion was filtered and used directly (see Table 3.5 for the amount used).

3.6 Preparation of buffer solution

3.6.1 Preparation of 0.44 M KH_2PO_4 and Na_2HPO_4 buffer solution pH 6.0-8.0

KH_2PO_4 (29.86 g, 0.219 mole) was dissolved in DI water (500 mL) and kept as stock solution 'Part A'. Na_2HPO_4 (39.07 g, 0.219 mole) was separately dissolved in DI water (500 mL) and kept as stock solution 'Part B'.

Table 3.3 Volume of the stock solution Part A and B for making a buffer solution of the required pH values of 6.0-8.0.[11]

pH	Part A	Part B
6.0	88.9	11.1
7.0	41.3	58.7
8.0	3.7	96.3

Note : Part A + Part B = buffer stock solution 100 mL

Note : [a] Refer to TDDT work instruction No. 14-06-028 (1999).

3.6.2 Preparation of 0.44 M disodium citrate and sodium hydroxide buffer solution pH 6.0-6.5

3.6.2.1 Preparation of 0.44 M disodium citrate solution

Citric acid monohydrate ($C_6H_8O_7.H_2O$) (92.67 g) was dissolved in DI water (1 L) and 4.4 M NaOH solution (200 mL) was then added. The solution was mixed and kept as stock solution 'Part A'.

3.6.2.2 Preparation of 0.44 M sodium hydroxide solution

Sodium hydroxide (17.60 g) was dispersed in DI water (1 L) and the solution was then kept as stock solution 'Part B'.

Table 3.4 Volume of the stock solutions Part A and B for making a buffer solution of the required pH values of 6.0-6.5. [11]

pH	Part A	Part B
6.0	60.3	39.7
6.5	54.0	46.0

Note : Part A + Part B = buffer stock solution 100 mL

3.7 Preparation of acid and alkaline solution

3.7.1 Preparation of 0.1 M sulfuric acid solution

95% sulfuric acid (5.6 mL) was pipetted into DI water (500 mL) in 1000 mL volumetric flask. Solution was made up volume to 1000 mL by DI water.

3.7.2 Preparation of 25% (13.4 M) and 0.1 M ammonia solution

Ammonia solution (25%, 13.4 M) can be directly used by slowly dropping into slurry. For 0.1 M of concentration, 25% (13.4 M) ammonia solution (7.5 mL was pipetted into DI water (500 mL) in 1000 mL volumetric flask. Solution was made up volume to 1000 mL by DI water.

3.8 Preparation of green phosphor slurry (beaker-scaled)

3.8.1 Slurry composition and preparation method[a]

Table 3.5 Composition of about 2 L green slurry

Composition	Quantity (g)	Individual pH value at 24 ± 2°C
1. Green phosphor powder	500	-
2. DI water	753	6.5
3. 8.5% PVA solution	441	5.1
4. 10% ADC solution	19.9	7.5
5. 5% pluronic solution	13.4	5.0
6. 5% tamol solution	29.9	11.0
7. 5% alscoap solution	26.9	7.0
8. 45% acrylic emulsion	45.0	9.1

Note : [a] Refer to TDDT engineering instruction No. 14-22-173 (1999).

Green phosphor powder (500 g) was dispersed in DI water (753 g). PVA solution (441 g) was then added and vigorously stirred. ADC solution (19.9 g) was added and the surfactant Nos. 5-8 as listed on Table 3.5 were then added, respectively. The mixture was thoroughly stirred for 12-15 hours. The specific gravity and viscosity of slurry were measured and recorded. Finally, the slurry was filtered and kept in a slowly stirred mixture before coating.

3.8.2 Slurry quality measurement

3.8.2.1 Specific gravity measurement method[a]

Blank gravimeter was weighed and recorded. Slurry was filled into gravimeter without bubbles until overflown and then the lid was covered. The overflown slurry part was wiped out. Then slurry with gravimeter was weighed and recorded.

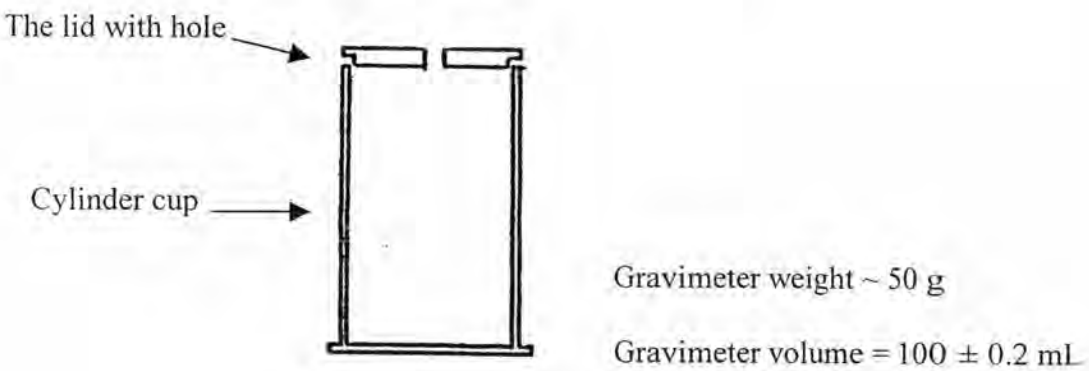

Figure 3.2 PVC gravimeter for specific graviiy measurement

Note : [a] Refer to TDDT work instruction No. 14-06-019 (1989).

Specific gravity (SG) can be calculated as follow.

$$SG = \frac{(\text{Gravimeter weight} + \text{Slurry weight}) - \text{Gravimeter weight}}{\text{Gravimeter volume}}$$

3.8.2.2 Viscosity measurement method[a]

The slurry was slowly poured into a ZAHN cup until full and the time was started measuring of the flowing slurry from point A to point B (the point that slurry stopped flowing and dropped). The resultant flow-time was recorded as viscosity in second unit (sec.). Measurement was repeated 3 times and averaged.

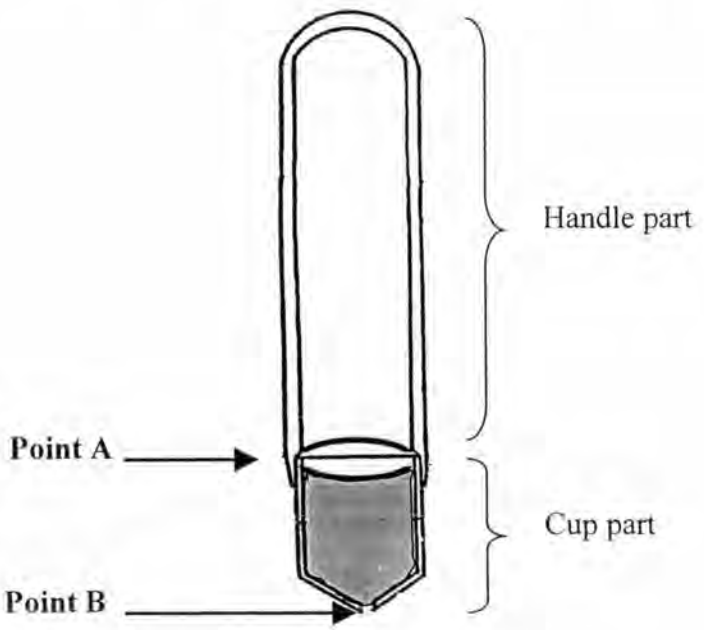

Figure 3.3 ZAHN cup for viscosity measurement

Note : [a] Refer to TDDT work instruction No. 14-06-020 (1989).

Table 3.6 Required specific gravity and viscosity of green slurry before coating[a]

Items	Required value
Specific gravity	1.278 ± 0.005
Viscosity (sec.)	40.2 ± 1.0 (19.7 ± 0.4 cps)*

Note : * The value in parenthesis was measured by Brookfield type viscometer, Toki RC-100.

3.8.3 Slurry quality adjustment

Slurry was adjusted when the specific gravity and viscosity value were not met the specification by adding a little amount of the following materials.

Table 3.7 Slurry adjustment reference[b]

SG	Viscosity	Adjusted by adding
OK	High	DI water, phosphor
OK	Low	Undiluted solution*
High	OK	DI water, diluted solution#
High	High	DI water
High	Low	Undiluted solution
Low	OK	Phosphor
Low	High	Phosphor and DI water
Low	Low	Phosphor and undiluted solution

Notes : * Undiluted solution means the slurry composition without DI water (no phosphor).

Diluted solution means the slurry composition with DI water (no phosphor).

Notes : [a] *Refer to TDDT engineering instruction No. 14-22-100 (2000).*

[b] *Refer to TDDT work instruction No. 14-2-112 (1995).*

After adjustment, slurry was further stirred for 30 minutes and finally was filtered.

3.9 Slurry coating and exposure[a]

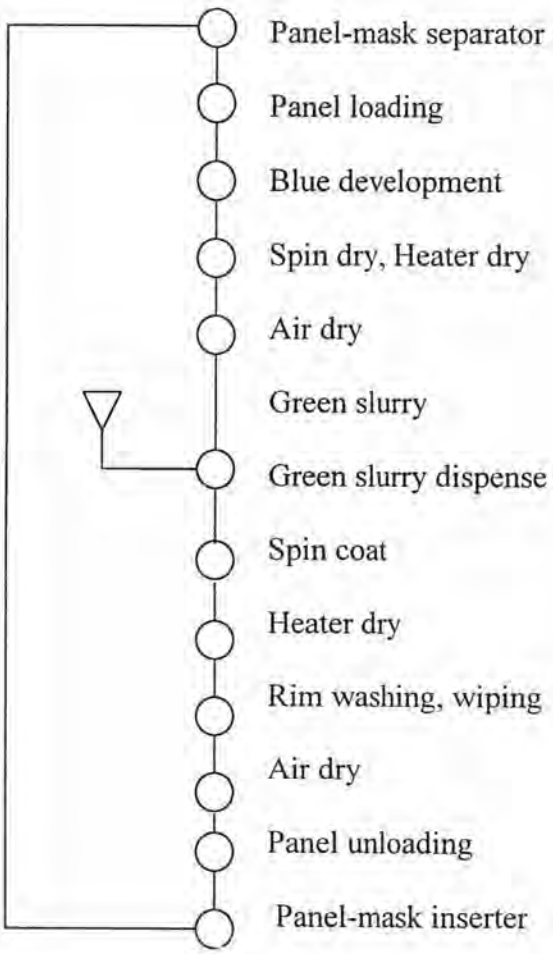

Figure 3.4 Flow chart of green slurry coating process

The panel and the mask were separated. The panel was loaded and developed for unexposed blue phosphor by spraying DI water then was spin dried

Note : [a] Refer to TDDT engineering instruction No. 14-2-0 (1998).

and heater dried. The slurry (~30 mL) was manually dispensed into the panel and the panel was then spun for a complete coating. The overflown slurry was discarded, and the panel was heater dried, rim washed and wiped. Finally, the panel was air dried and unloaded to exposure process.

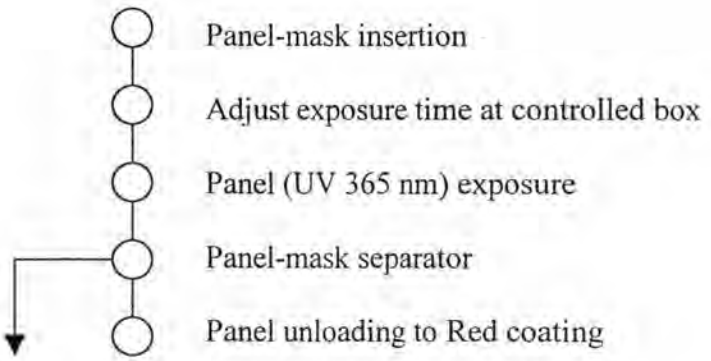

Figure 3.5 Flow chart of green exposure process

The coated panel was loaded to the panel-mask insertion machine. The exposure time was manually adjusted as required in Table 3.8. The panel was automatically loaded and exposed as required time. Finally, its mask was separated before red coating and going towards the back process.

Table 3.8 Required exposure time adjusted for each experiment

%Exposure quality * (% EQ)	EQ # ($mW.sec/cm^2$)	Intensity (mW/cm^2)	Time adjust (sec)
115%	3405	75	45.4
100 %	2692	75	39.5
85%	2520	75	33.6
70%	2070	75	27.6

Notes : * 100% EQ equals to routine mass production's exposure condition

EQ or Exposure quality = Intensity (mW/cm^2) X Time (sec.)

3.10 Slurry pH adjustment

3.10.1 Adjusted by using buffer solutions

Each buffer solution was used in place of DI water to meet required slurry pH values. According to slurry preparation method in section 3.8.1 and composition shown in Table 3.9, DI water was replaced by the corresponding buffer solution and proceeded as aforesaid method.

Table 3.9 Composition of about 2 L buffered slurry

Component	Quantity (g)				
	pH 6.0	**pH 6.8**	**pH 7.0**	**pH 7.5**	**pH 8.0**
1. Green phosphor powder	500	500	500	500	500
2. Buffer solution*	753	753	753	753	753
3. 8.5% PVA solution	441	441	441	441	441
4. 10% ADC solution	19.9	19.9	19.9	19.9	19.9
5. 5% pluronic solution	13.4	13.4	13.4	13.4	13.4
6. 5% tamol solution	29.9	29.9	29.9	29.9	29.9
7. 5% alscoap solution	26.9	26.9	26.9	26.9	26.9
8. 45% acrylic emulsion	45.0	45.0	45.0	45.0	45.0

Note : * The buffer solutions were 1) 0.44 M KH_2PO_4 and Na_2HPO_4 solution (pH 6.0,7.0 and 8.0) for the corresponding slurry pH 6.0, 7.0 and 8.0, respectively and 2) 0.44 M disodium citrate and sodium hydroxide solution (pH 6.0 and 6.5) for the corresponding slurry pH 6.8 and 7.5, respectively.

3.10.2 Adjusted by reducing tamol solution

% Tamol solution (against PVA) was reduced to 90%, 70% and 50%, respectively. Preparation method was similar to section 3.8.1 but composition was changed as shown in Table 3.10.

Table 3.10 Slurry composition in the reduction of % tamol experiment

Composition	Normal 100% tamol	90% tamol	70% tamol	50% tamol
1. DI water	753	756	762	768
2. Phosphor	500	500	500	500
3. 8.5% PVA solution	441	441	441	441
4. 10% ADC solution	19.9	19.9	19.9	19.9
5. 5% pluronic	13.4	13.4	13.4	13.4
6. 5% tamol	29.9	26.9	20.9	15.0
7. 5% alscope solution	26.9	26.9	26.9	26.9
8. 45% acrylic emulsion	45.0	45.0	45.0	45.0
Final slurry pH	8.2	7.8	7.8	7.8

3.10.3 Adjusted by using sulfuric acid and ammonia solution

3.10.3.1 The 1st slurry composition used in the 1st and 2nd experiments

Sulfuric acid (0.1 M) was added dropwise into stirred slurry with the composition shown in Table 3.11 until the required pH values were obtained. Four mixtures were prepared separately for the required pH values of 6.0, 6.5, 7.0, 7.5, respectively.

Ammonia solution (25%, 13.4 M) was added dropwise into stirred slurry (Table 3.11) until the required pH values were obtained. Two mixtures were

prepared separately for the required pH values of 8.5 and 9.0. No pH adjustment was necessary for the slurry pH 8.2.

Table 3.11 The 1st slurry composition used in the 1st and 2nd experiment using sulfuric acid and ammonia solution for pH adjustment

Component	Quantity (g)						
	pH 6.0	**pH 6.5**	**pH 7.0**	**pH 7.5**	**pH 8.2**	**pH 8.5**	**pH 9.0**
1. Green phosphor powder	500	500	500	500	500	500	500
2. DI water	753	753	753	753	753	753	753
3. 8.5% PVA solution	441	441	441	441	441	441	441
4. 10% ADC solution	19.9	19.9	19.9	19.9	19.9	19.9	19.9
5. 5% pluronic solution	13.4	13.4	13.4	13.4	13.4	13.4	13.4
6. 5% tamol solution	29.9	29.9	29.9	29.9	29.9	29.9	29.9
7. 5% alscoap solution	26.9	26.9	26.9	26.9	26.9	26.9	26.9
8. 45% acrylic emulsion	45.0	45.0	45.0	45.0	45.0	45.0	45.0
9. 0.1 M sulfuric acid	94	68	37	13	0	0	0
10. 25% NH_3 solution	0	0	0	0	0	0.5	0.8

3.10.3.2 The 2nd slurry composition used in the 3rd experiment

Sulfuric acid (0.1 M) or ammonia solution (0.1 M) was added into stirred slurry which was composed of components 1-8 as shown in Table 3.12. The pH values (acidity range) were then measured. In this experiment, the amount of DI

water was reduced to give the constant sum amount with the sulfuric or ammonia solution equaling to 753 mL.

Table 3.12 The 2nd slurry composition used in the 3rd experiment

Component	Quantity (g)			
	pH 6.2	**pH 7.1**	**pH 8.2**	**pH 9.0**
1. Green phosphor powder	500	500	500	500
2. DI water	659	716	753	646
3. 8.5% PVA solution	441	441	441	441
4. 10% ADC solution	19.9	19.9	19.9	19.9
5. 5% pluronic solution	13.4	13.4	13.4	13.4
6. 5% tamol solution	29.9	29.9	29.9	29.9
7. 5% alscoap solution	26.9	26.9	26.9	26.9
8. 45% acrylic emulsion	45.0	45.0	45.0	45.0
9. 0.1 M sulfuric acid	94	37	0	0
10. 0.1 M NH_3 solution	0	0	0	107

3.11 Screen quality inspection

After all 3 slurries (blue, green and red) were coated and processed, screen quality was inspected before loading to the other process.

3.11.1 Dot size inspection

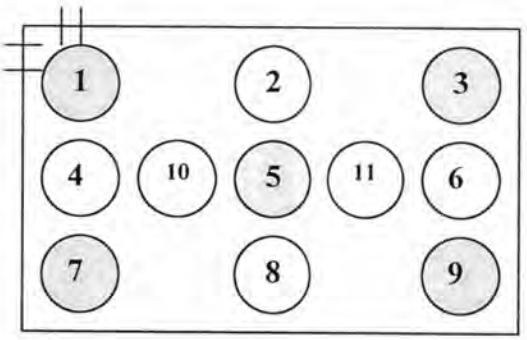

Figure 3.6 Panel positions for screen quality inspection[a]

Positions 1,3,7,9 (corner area) and 5 (center area) were used for dot size inspection. The sizes of five dots from each area were measured by using shop micrometer 80X and averaged. The reading values were recorded in micron unit.

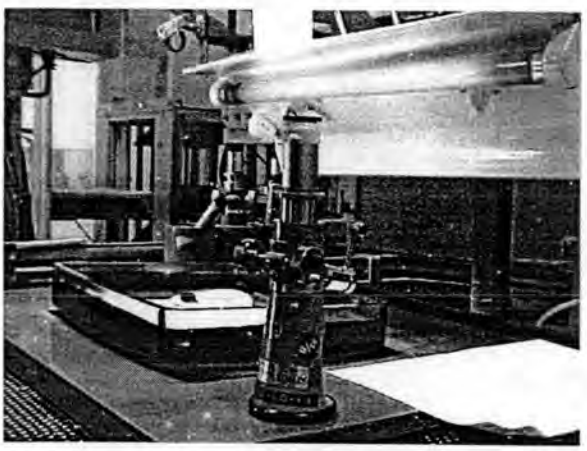

Figure 3.7 Shop micrometer under UV light on an inspection table

Note : [a] *Refer to TDDT work instruction No. 14-31-095 (1999).*

3.11.2 Other qualities inspection

3.11.2.1 Color purity

The color purity was inspected by using an XY analyzer. The panel outside was inspected and automatically read by this instrument. All panel positions shown in Figure 3.6 were read and recorded.

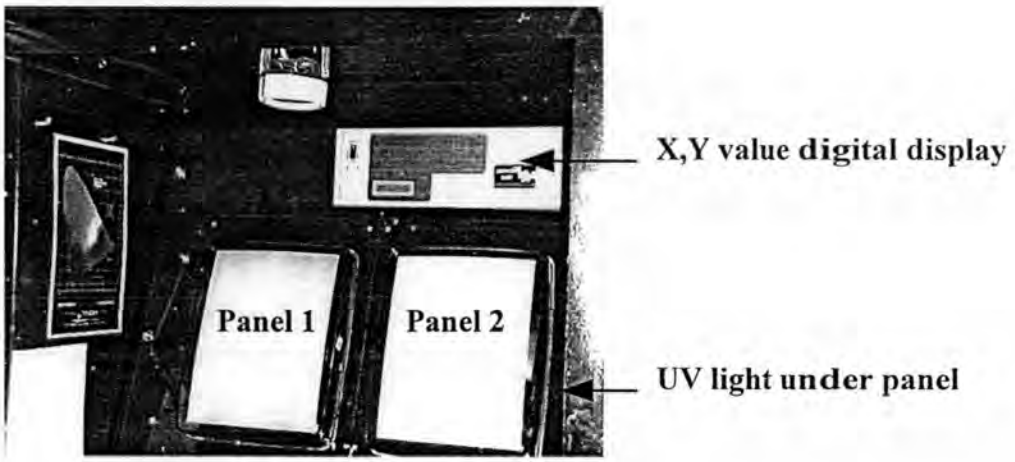

Figure 3.8 Color XY analyzer

3.11.2.2 Pin hole inspection

Dot's pin hole was inspected under UV light by using shop micrometer 80X. Pin hole ranks are shown in Figure 3.9.

Rank A	**Rank A^-, B^+or B^-**	**Rank C**
No hole	Few holes	Many holes inside dot

Figure 3.9 Pin hole appearance for rank judgement[a]

Note : [a] *Refer to TDDT engineering instruction No. 14-2-0 (1998).*

3.11.2.3 Sharpness inspection

Dot's sharpness was inspected inside the panel under UV light by using shop micrometer 80X. Sharpness ranks are shown in Figure 3.10.

Rank A **Rank A^-, B^+,B^-** **Rank C**

Figure 3.10 Dot's sharpness appearance for rank judgement[a]

3.11.2.4 Other qualities inspection

Phosphor film adherence, bubbles inside or other impurities on the film, white uniformity (WU) level, field light output (FLO), color analysis, corner brightness (CB) were inspected.

Note : [a] Refer to TDDT work instruction No. 14-05-098 (1999).