

# CHAPTER IV

## EXPERIMENTAL WORK

The experimental works on polyurethane coating presented here consist of four parts. In the first part, eight acrylic polyols are synthesized to study three effects, hydroxyl value (OHV), molecular weight (MW) in term of the amount of catalyst and acid value (AV). Then in the second part, the following properties of polyols will be examined: non volatile content (NV), viscosity, acid value (AV), molecular weight and molecular distribution by gel permeation chromatography (GPC). In the third part the polyurethane film preparation will be demonstrated. The clear sixteen lacquer films are prepared by matching eight acrylic polyols with two hardeners, NBDI and IPDI isocyanurate. Finally, the physical film properties will be tested on hardness, bending, dupont impact, acid-base resistance, drying time, weatherability, tensile strength and dynamic mechanical test.

### **1.Synthesis acrylic polyol.**

Eight polyols will be synthesized in order to study the following three effects, hydroxyl value (OHV), molecular weight (MW) in term of the quantity catalyst and acid value (AV). Varying the quantity of hydroxyl monomer and acid monomer can change the hydroxyl value and acid value, respectively. The three effects will be varied in two values, consequently eight polyols are different in composition. The composition of polyols will be shown in table 4.1.

All of the polyols will be synthesized in the same way. Firstly, the solvent (Toluene and i-Butyl Acetate) is filled in a round bottom reaction flask and heated in the reaction temperature ( 98 ° C). Then the mixed monomer and catalyst is charged continuously into the flask. In the first hour 40% of the mixed monomer is fed. The remaining 60% is charged within 4 1/2 hours. After that the reaction is kept at the constant temperature for 1 1/2 hours. Then cooling down to lower temperature (85 ° C) is required before the additional catalyst is filled for post polymerization to the complete reaction. In this reaction, three post polymerizations are necessary. In the first and the second post polymerization, the flask temperature are kept at 90 ° C for 1 hour. The last post polymerization, the flask temperature is kept at elevated temperature for three hour at 90-95 ° C, 95-100 ° C and 100-110 ° C respectively (one hour at each temperature). The final product is produced after cooling and adjusting the non-volatile content by adding the solvent.

**Table 4.1. Composition of monomer (%) and Quantity of catalyst (% in part of monomer)**

Basis:  $T_g^5 = 10.13^\circ \text{C}$  is constant all of polyol

Polyol no.	Acrylic monomer							Catalyst
	MMA	n-BMA	EA	n-BA	HEA <sup>2</sup>	Mac <sup>3</sup>	DMAEMA	AIBN <sup>4</sup>
#3	39.04	10.00	18.79	18.79	12.59	0.49	0.31	0.31
#4	38.56	10.00	18.79	18.78	12.59	0.98	0.31	0.31
#5	39.04	10.00	18.79	18.79	12.59	0.49	0.31	0.61
#6	38.56	10.00	18.79	18.78	12.59	0.98	0.31	0.61
#7	38.22	10.00	18.79	15.66	16.54	0.49	0.31	0.31
#8	37.74	10.00	18.79	15.65	16.54	0.98	0.31	0.31
#9	38.22	10.00	18.79	15.66	16.54	0.49	0.31	0.61
#10	37.74	10.00	18.79	15.65	16.54	0.98	0.31	0.61

<sup>5</sup>  $T_g$  calculation can be seen in appendix C

Note : <sup>2</sup>HEA is hydroxyl monomer.

<sup>3</sup>MAc is acid monomer.

<sup>4</sup>AIBN is catalyst. (AIBN-R product of Japan Hydrazine Company)

For more convenience each factor is noted in low (-1) and high (+1) value to understand the combination of effect in each polyol.

**Table 4.2 Eight polyols with three effects.**

Polyol	OHV	Cat	AV
3	-1	-1	-1
4	-1	-1	+1
5	-1	+1	-1
6	-1	+1	+1
7	+1	-1	-1
8	+1	-1	+1
9	+1	+1	-1
10	+1	+1	+1

**Note :** OHV (-1) = 60 mg KOH/g of resin

OHV (+1) = 80 mg KOH/g of resin

Catalyst (-1) = 0.31 % part of monomer (MW<sup>5</sup> = 110,000-140,000)

Catalyst (+1) = 0.61 % part of monomer (MW = 60,000-80,000)

AV (-1) = 2.0-2.2 mg KOH/g of resin

AV (+1) = 3.4-3.6 mg KOH/g of resin

<sup>5</sup>The actual value of molecular weight (MW) in each polyol can be seen in Appendix A.

## Polyol #3

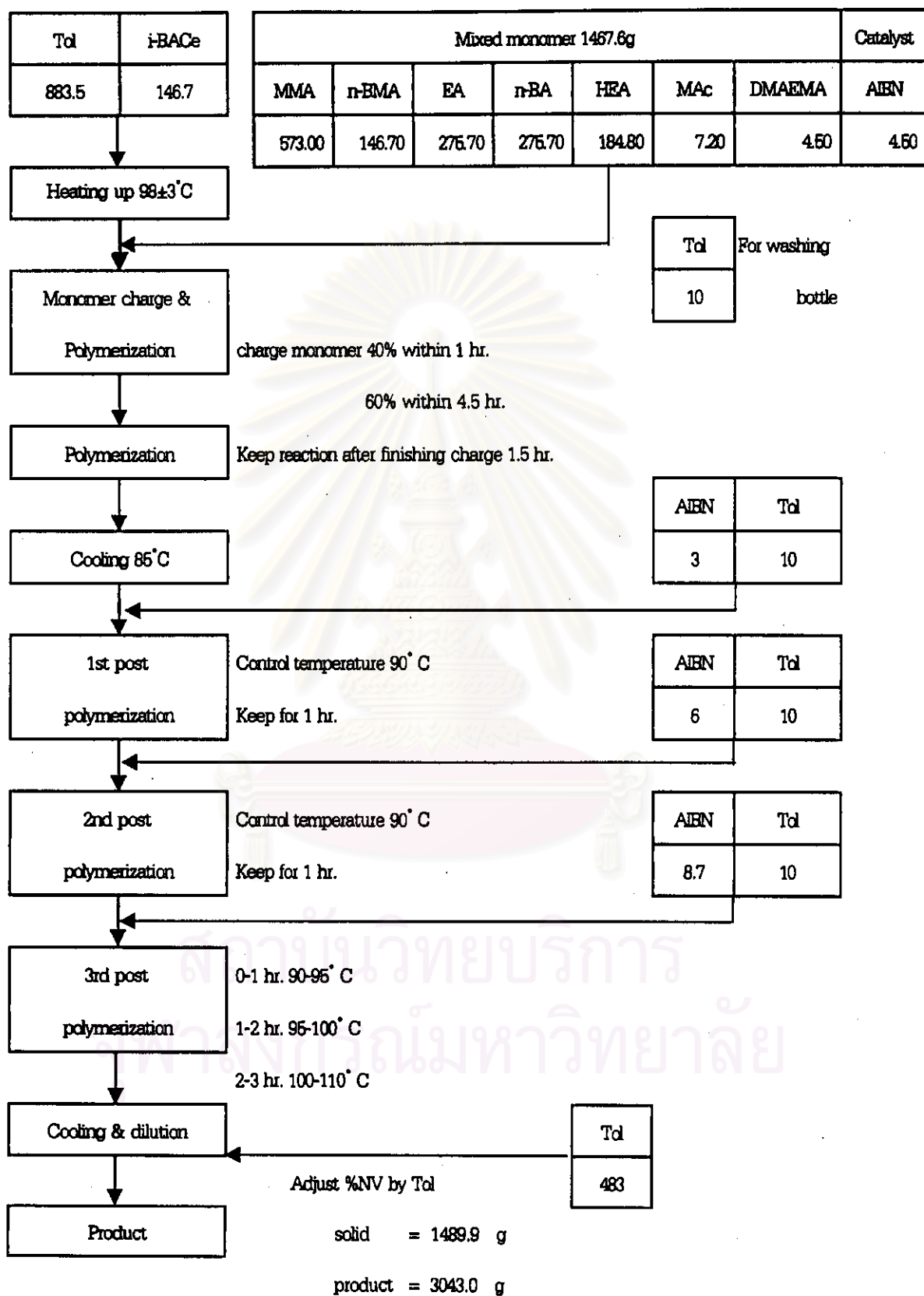


Figure 4.1 Synthesis polyol diagram

## 2. Determine Properties of the Polyols.

There are four items of specification determined here namely: non volatile matter (NV), gardner viscosity, acid value and molecular weight by gel permeation chromatography (GPC). Each of them will be described as follows.

### 2.1 Non volatile matter

#### Apparatus:

1. Hot air oven with circulating rotary
2. Aluminium foil pan
3. Dessiccator
4. Clip
5. Balance with four decimals.

#### Procedure:

1. Open the oven and set temperature at 150°C .
2. Accurately weigh an aluminium pan with one clip at least four decimals.
3. Fill the sample 1.5 g approximately in aluminium pan.
4. Spread the sample on the foil by clip. So that the sample thickness becomes equally.
5. Three samples are necessary.
6. Put prepared samples in oven and keep them for 20 minutes.
7. After baking, move samples to desiccator until they are cool. Accurately weigh all samples again.

$$\text{Nonvolatile matter (\%)} = \frac{\text{Weight of resin after drying (g)} \times 100}{\text{Weight of resin before drying (g)}} \quad (4-1)$$



## **2.2 Viscosity by Gardner**

Gardner viscometer is used to measure the relative viscosity by comparing the bubble rising speed of the sample in the viscosity tube with a standard tube.

### **Apparatus:**

1. Standard viscosity tube set from A to Z10
2. Viscosity tube for measurement.
3. Thermostatic water bath ( $0.5^{\circ}\text{C}$  accuracy)
4. Holding frame for viscosity tube

### **Procedure:**

1. Set the thermostatic water bath to  $25^{\circ}\text{C}$ .
2. Fill sample to viscosity tube for measurement.
3. Immerse the sample tube and standard viscosity tube set in the thermostatic water bath. Keep at least 30 minutes for the sample reach  $25^{\circ}\text{C}$ .
4. Compare the bubble velocity of sample tube with the standard tubes.

The viscosity of the sample is determined by the number of the standard viscosity tube nearest to the rising speed of foam sample.

## **2.3 Acid Value Test (AV)**

This is to determine the reactivity of carboxyl group in the resin by expressing the acid value in the weight (mg) of potassium hydroxide required for neutralization of acid content in 1 g of the sample.



**Apparatus:**

1. Buret
2. Erlenmeyer flask

**Reagents:**

1. Phenolphalein solution 1% (w/v)
2. 0.1 normal Ethanol potassium hydroxide solution
3. Xylene and n-butanol mixed solution by ratio = 1:1

**Procedure:**

1. Weigh the sample 5 g (2 decimal) in an erlenmeyer flask.
2. Add 20-30 ml. of mixed solution of Xylene & n-Butyl Alcohol to the flask and mix together until the sample dissolves.
3. Add 2 drops of phenolphthalein solution as an indicator.
4. Titrate the solution with 0.1 N KOH. The end point is detected when the colour of the solution turns to be pink.

$$AV = \frac{V1 \times F1 \times 5.61}{M1} \quad (4-2)$$

V1 = The amount of 0.1 N KOH solution, ml

F1 = The factor of 0.1 KOH solution

M1 = The sample weight, g

**2.4 Gel Permeation Chromatography (GPC)**

Gel permeation chromatography (GPC) is one of the chromatographic techniques which uses highly porous, non-ionic gel beads for the separation of polydisperse polymers in solution. The largest macromolecules of the solute cannot penetrate the pores within the crosslinked gel beads, and thus elute first (their retention time is shorter). The smallest macromolecules of the solute are

retained in interstices within the gel beads and therefore require more time to elute (their retention time is longer).

Using this technique, molecular weight of polyol will be known as number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ). Molecular weight distribution of polyol will be also calculated in term of polydispersity index ( $M_w/M_n$ )



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### 3.Film preparation.

In this work, the clear lacquer will be coated on the substrate. The free pigment or clear lacquer consists of three parts: thinner, resin or acrylic polyol and hardener. The quantity of thinner added on the lacquer depends on the suitable viscosity which is different in each application method. Unlike thinner, polyol and hardener react with each other exactly in 1:1 mole ratio. Then the three components are mixed together completely. The lacquer is coated by bar coater on the bondelite plate and the obtained thickness must be controlled at 25-30  $\mu\text{m}$ . After that, the curing process is accelerated by baking in the oven. After baking, the films are kept 1 week at room condition for complete curing before testing the film properties.

The notation of samples used in this report consists of two alphabets, the first is polyol and the second is hardener.

**Table 4.3. The notations of samples**

<i>Sample</i>	<i>Polyol</i>	<i>Hardener</i>	<i>Sample</i>	<i>Polyol</i>	<i>Hardener</i>
3N	#3	NBDI	3I	#3	IPDI
4N	#4	NBDI	4I	#4	IPDI
5N	#5	NBDI	5I	#5	IPDI
6N	#6	NBDI	6I	#6	IPDI
7N	#7	NBDI	7I	#7	IPDI
8N	#8	NBDI	8I	#8	IPDI
9N	#9	NBDI	9I	#9	IPDI
10N	#10	NBDI	10I	#10	IPDI

### 3.1 Condition of film preparation

- Resin = Acrylic polyol #3-#10
- Hardener = NBDI and IPDI isocyanurate
- NBDI isocyanurate = Mitsui Chemical 's product
- IPDI isocyanurate = VESTANAT T1890/100 Huls 's product
- Resin : Hardener<sup>2</sup> = 1 : 1 in mole ratio
- Thinner = Xylene : Toluene : Butyl Acetate : Cellosolve Acetate.  
3 : 3 : 2 : 2
- Coating method = Bar coater
- Substrate = Bondelite Plate (JIS G 3141) thickness 0.6 mm
- Curing condition = Bake at 70°C, 30 minute.
- Post curing = 7 days.
- Thickness of film = 25-30 μm

### 3.2 Bar coater coating.

A bar coater<sup>3</sup> is a stainless steel bar of 6.35 mm. in diameter and 400 mm. in length, wrapped without clearance with a wire of stainless steel. Fix the test panel on an upper side of horizontal surface and spread the sample on the surface lower than the bar coater. While moving the bar coater, press the both ends with fingers of both hands so that the uniform force is applied on the whole body of bar coater and drawn to the other side of panel at a uniform speed.

<sup>2</sup> The quantity of NBDI and IPDI used with eight polyols are presented in the appendix A.

<sup>3</sup> The number of bar coater corresponding to required thickness is also demonstrated in the appendix C.

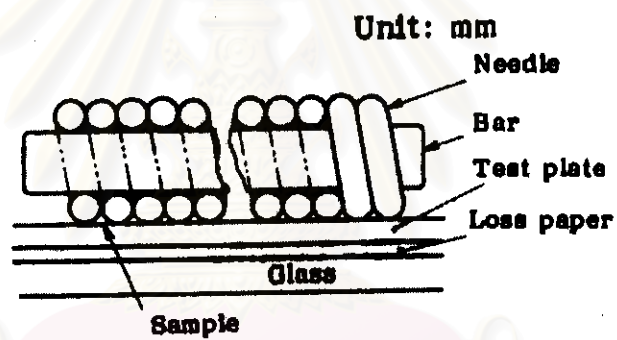
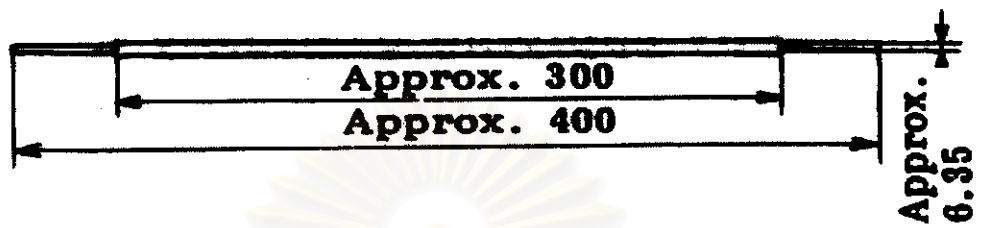


Figure 4.2 Bar coater

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#### **4. Film properties test.**

There are two kinds of film properties, one is from mechanical test and the other one is from physical test. The mechanical test is the test simulated from real service conditions of coatings. A variety of mechanical tests have been developed to measure such properties as hardness, flexibility, impact resistance etc. The tests are normally carried out with the coating intact on the substrate. The main purpose of carrying out such tests is to rank the performance of coatings prepared from the similar formulation. In contrast, the physical property determinations are carried out in all branches of material science. Normally, the physical property tests require free film. The result of these tests can relate between the film properties and structure of the macromolecule.

In this work, both of them will be tested. In the mechanical tests, the pencil hardness, bending or flexibility, Dupont impact resistance, acid and base resistance, drying time and weathering resistance are measured. In addition, the Dynamic Mechanical Analysis (DMA) test, tensile strength and elongation test are analyzed in the physical properties.

##### **4.1 Pencil hardness test (Hand Scratch method)**

To examine the hardness, paint film is scratched by scratching with core of pencil and express by the concentration of the symbol of pencil from 6B (softest) to 9H (hardest). A pencil used to measure the hardness of paint film is specified in JIS S 6006. The Mitsubishi pencil guaranteed by JIS is used in this work.

Hold the pencil at an angle of approximately  $45^{\circ}$  and press the coating surface as strongly as possible at a uniform speed. Repeat the test three times

and evaluate the film. If not less than one of flaw occurs, this concentration symbol pencil will be recorded.

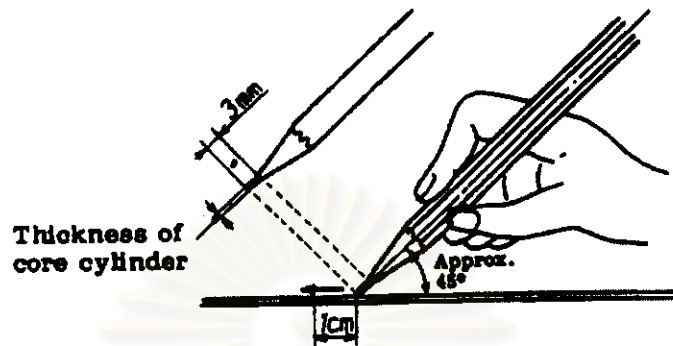


Figure 4.3 Pencil Hardness Test.

#### 4.2 Bending test (Flexibility)

This method examines the cracking resistance when bending the test specimen coated with paint film by measuring the bending angle of the plate until the film cracks. The bending angle is determined by the number of core rod which is used to bend the plate around. A device is made up of a set of tester, core rod with definite diameter and auxiliary plate. The test piece is inserted between the foldable plate and core rod. The test piece then is bent around the core rod. The bending ability is subjected to the size of core rod that gives uncracked film.

Note: The auxiliary plate is used to adjust the thickness of receiving plate by matching to the thickness of respective thickness of core rods.

### Bending Tester

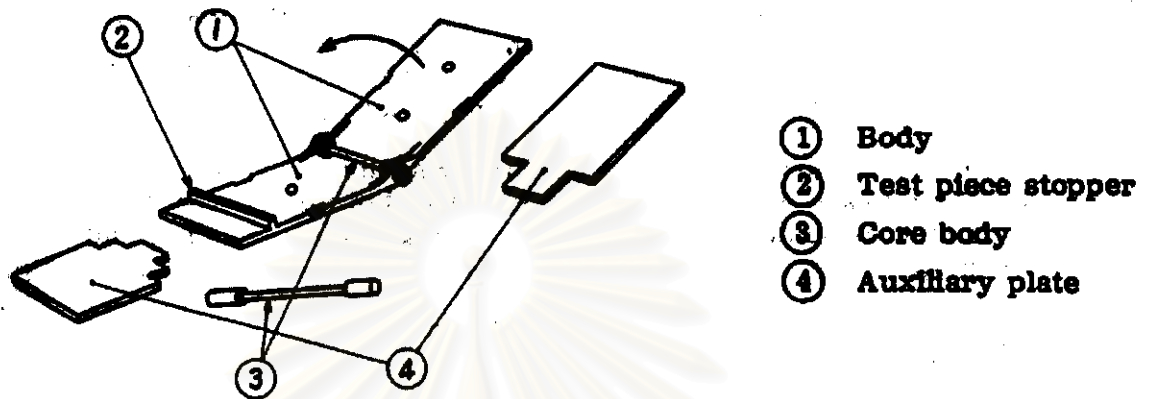


Figure 4.4 Bending Tester.

### 4.3 Dupont Impact test

This method is to test the resistance of impact of the films. The resistance is measured by the impact weight, the height of dropping weight and the diameter of indenter. The purpose of this test is to examine the cracking and peeling of paint film when the sphere body impacted on the surface of paint film by the shock resistance. A shock deformation tester constituted of indenter having a definite roundness at the top end, a receiving stand having depression matching to the roundness and a device to drop the weight from a definite height. In most tests, a weight is dropped down a guide tube onto a hemispherical indenter which rests on a coated panel. A hole below the panel opposite the indenter permits deformation of panel as well as the coating.



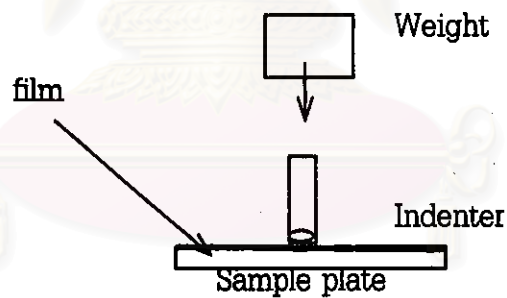
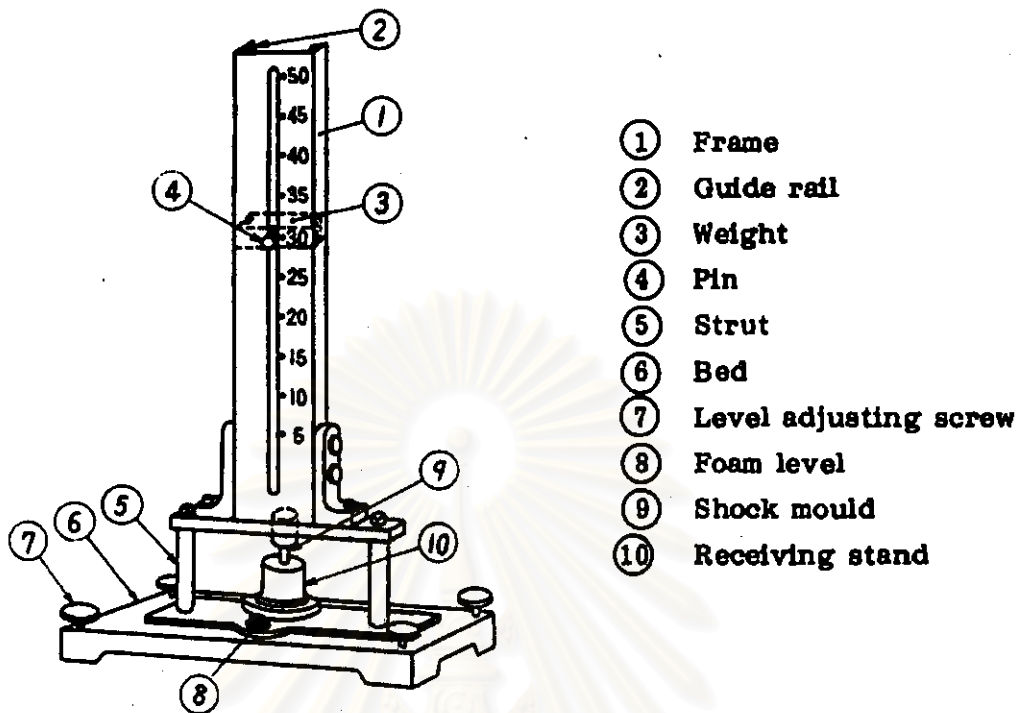


Figure 4.5 Dupont impact equipment

#### 4.4 Acid-Base Resistance test

Firstly, immerse the test piece in acidic or basic solution for 48 hours. After that the test piece is tested in Dupont impact, and compared with the result before dipping in acidic or basic solution. The resistance of coatings is



reported by the difference in height of Dupont impact before and after dipping solution.

**Acidic solution** : Sulphuric Acid ( $H_2SO_4$ ) 5 % w/v in deionized water.

**Basic solution** : Sodium Hydroxide (NaOH) 5 % w/v in deionized water.

#### **4.5 Drying Time**

After coating the paint, the viscosity increases until the film is formed. There are three values of drying time to define.

**1. Set to Touch ( $t_s$ )** is the time after coating when touching the middle part of coating surface lightly with a finger and the condition where the finger is not stained.

**2. Tack Free ( $t_t$ )** is the time after coating when rubbing gently at the middle part of the coating surface with finger lightly while the coating surface is free from rubbing trace.

**3. Dry Hard ( $t_d$ )** is the time after coating when place strongly at the middle part of coating surface between the thumb and forefinger, the condition where dent due to finger trace is not adhered. In the other word when rubbing quickly the middle part of coating surface with finger repeatedly, rubbing traces are not adhered on the coating surface.

#### 4.6 Gel time test

Similar to drying time test, the purpose of gel time test is to assess the reactivity of coating. The coating is prepared same as item 3.1 of this chapter after that it is diluted by thinner until every samples has the same viscosity, 30 seconds by ford cup #4. In the next step, all samples are measured the viscosity every 30 minutes until they are gel.

An Example of Ford Cup

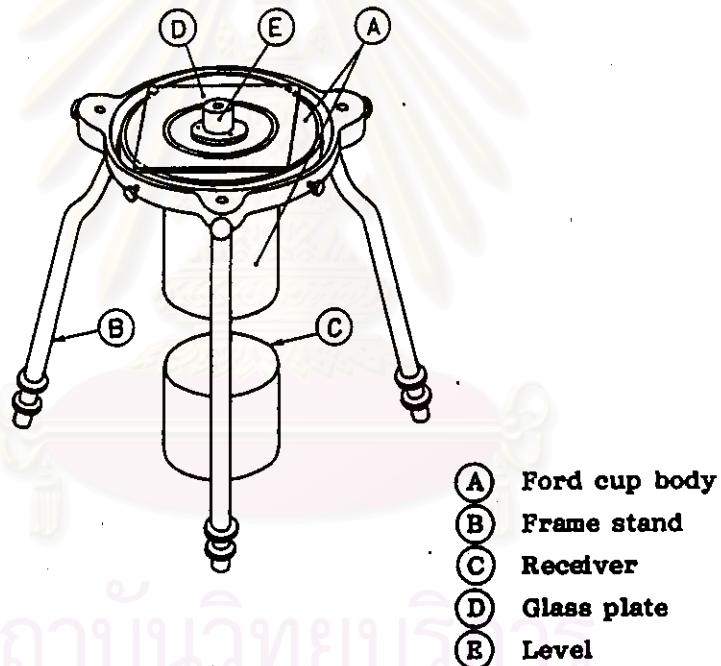


Figure 4.7 Ford cup no. 4 (JIS K5400)

#### **4.7 Weathering test.**

This test consists of two types, exposure test and QUV test. The exposure test is the test at real condition in long period of time. The QUV, accelerated weathering device, is the equipment simulating the service condition in the apparatus. The test panels are prepared in the same way for both tests. In the test panel preparing step, it is necessary to coat white base first because the gloss of the clear coating cannot be measured. Then the clear coat prepared from eight polyols with two hardeners (sixteen samples) are coated.

##### **The condition of test panel preparation**

- Base coat* :        -Uvan 20 N60 & Almatex 787 (3 : 7)  
                           (The product of Thai Mitsui Specialty Chemical)  
                           -PWC (Pigment Weight Content) = 50%  
                           -Pigment = Titanium Oxide  
                           -Thinner = Cellosolve Acetate : Solvesso #100 (2 : 1)  
                           -Curing condition = 140°C, 20 minute.  
                           -Dispersed by Paint Shaker 1 hour.
- Clear coat* :        -Polyol #3-#10 & NBDI, IPDI isocyanurate.  
                           -The method is the same as in section 3, Film preparation.

##### **4.7.1 Exposure Test**

The sixteen samples are exposed to the outdoor condition. The gloss at 60° of film is measured every two week. The result is analyzed in term of gloss retention. The gloss retention is determined as follows,

$$\text{Gloss Retention (\%)} = \frac{\text{Gloss}}{\text{Initial Gloss}} \times 100 \quad (4-3)$$

#### 4.7.2 QUV Test

This test is similar to the exposure test but it occurs in the simulating condition in order to accelerate the experiment. The cycle of test is in UV light for 8 hours and then water spray for 4 hours. The experiment is maintained in this cycle for 700 hours. Gloss and yellowness measurements are conducted every 200 hours.

#### Details of equipment

- Model** : UV-CON MODEL UC-1 (ATLAS DELECTRIC DEVICES)  
**Condition** : UV light 8 hours and Water spray 4 hours in cycle.  
**Light Source** : Special fluorescent lamp (ASTM G53)

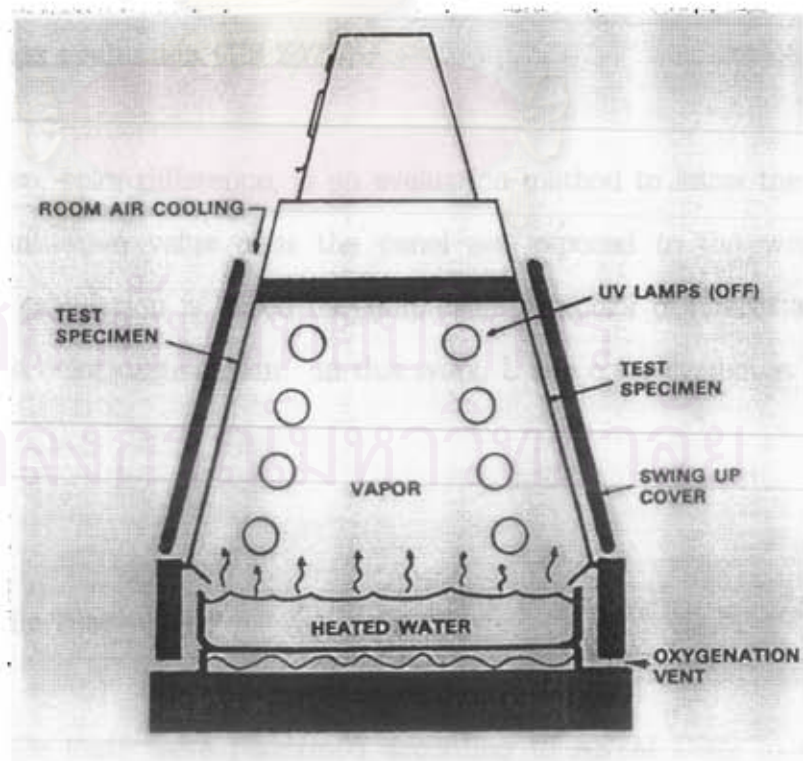
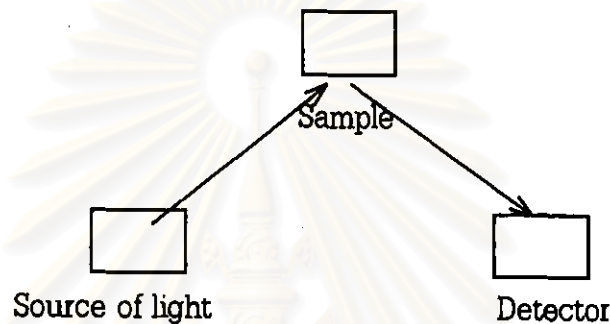


Figure 4.8 QUV machine

### **Gloss measurement (JIS Z8741)**

Gloss meter is the equipment for measuring the glossy by reflection of the light at various angles. The simple meter is presented below. The meter shows the quantity of glossy by the percent of light reflection. The angles of reflection are  $20^{\circ}$ ,  $60^{\circ}$  and  $85^{\circ}$ . The angle selection depends on the type of coating. The chosen angle in this work is  $60^{\circ}$ .



**Figure 4.9 The Gloss meter**

### **Yellowness evaluation (JIS Z8730)**

Yellowness, color difference, is an evaluation method to know the change of color in quantitative value after the panel are exposed to the weathering condition. The calculation is based on comparison the color of film at any time relating with the color original film. In this work, L a b color system is used as basis.

### **4.8 Tensile Test**

The tensile tests were performed according to ASTM D882 to measure tensile strengths and elongations by using OREINTEC TENSILON RTA-500

machine. The film is prepared by coating on the polypropylene plate by applicator. The thickness of film is controlled at 50-100  $\mu\text{m}$  and can be varied  $\pm 10\%$  of the maximum thickness. The test pieces are cut to rectangular shapes of 10 x 50 mm. Both sides of specimen, 10 mm in length, are held by grips. The initial length between grips is 30 mm. Each specimen is visually checked to be free of flaws or imperfect cutting edges. The test temperature is  $23 \pm 2^\circ\text{C}$ . The rate of separation grips is constant at 3 mm/min.

$$\text{Tensile Strength} \quad = \quad \frac{\text{Maximum load (kg}_f\text{)}}{\text{Cross section area (cm}^2\text{)}} \quad (4-4)$$

$(\text{kg}_f/\text{cm}^2)$

$$\text{Elongation (\%)} \quad = \quad \frac{\text{Elongation at break (mm)} \times 100}{\text{Original length (30 mm)}} \quad (4-5)$$

at break

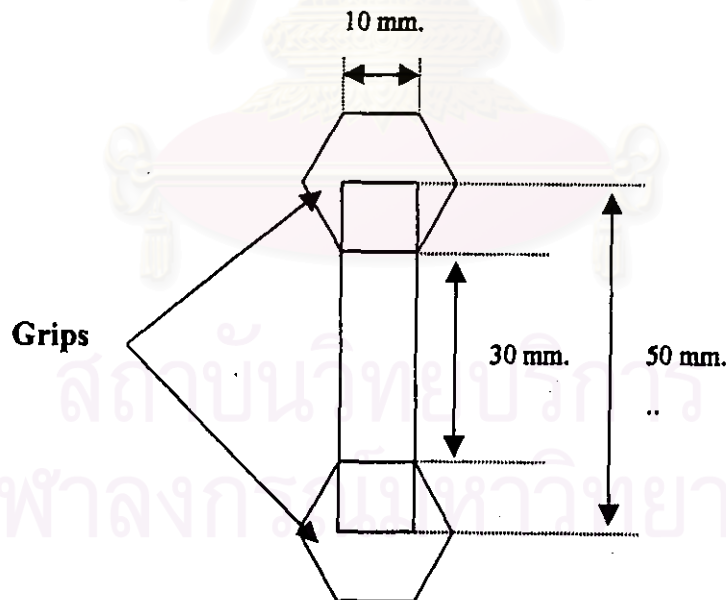


Figure 4.10 Tensile test piece