



## CHAPTER III

### APPARATUS AND EXPERIMENTAL METHODS

#### Materials

##### 1. Suspension PVC Resin

(Thai Plastics and Chemicals Co., Ltd.)

Suspension PVC Resin PVC-103      K-Value 60

Suspension PVC Resin PVC-104      K-Value 65

Suspension PVC Resin PVC-106      K-Value 70

##### 2. Plasticizer

(TOA Plasticizer Industries Co., Ltd.)

Dioctyl Phthalate ( $C_{24}H_{38}O_4$ )

Molecular Weight                      390

Viscosity at 30°C                      43 cps.

Specific Gravity at 20°C              0.986

##### 3. Heat Stabilizer

(Hacros Co., Ltd.)

Ba-Cd-Zn Complex liquid stabilizer

Viscosity at 25°C                      50 cps.

Specific Gravity at 20°C              1.03

**4. Co-stabilizer**

(Akzo Chemical Co., Ltd.)

Epoxydized Soybean Oil

Viscosity at 20°C                      400 cps.

Specific Gravity at 20°C              0.99

**5. Lubricant**

(Imperial Industrial Chemicals Co., Ltd.)

Stearic acid

Molecular Weight                      284.47

Melting Point                              69.3 °C

Specific Gravity                            0.847

**6. Filler**

(Surin Omya Chemicals (Thailand) Co., Ltd.)

Stearic acid coated CaCO<sub>3</sub>

Bulk Density                                1.20 g/cc.

Specific Gravity                            2.70

Mean Particle Size                        3.50 micron

**7. Fire retardant**

(Alcan Chemicals)

Zinc hydroxystannate, Flamtard H, (Zn Sn (OH)<sub>6</sub>)

Zinc stannate, Flamtard S, (ZnSnO<sub>3</sub>)

**Table 3-1 Properties of zinc hydroxy stannate and zinc stannate (7)**

Properties	Flam t ard H	Flam t ard S
Decomposition temperature (°C)	200	> 300
Median particle size(μm)	< 2	1.7
Density(g/cm <sup>3</sup> )	3.3	3.9
Whiteness	85	87
Oil absorption value(g/100g)	-	25

Antimony trioxide (Sb<sub>2</sub>O<sub>3</sub>)

(Cookson Ceramics and Antimony Limited)

**Table 3-2 Properties of antimony trioxide (8)**

Total antimony content(as Sb <sub>2</sub> O <sub>3</sub> )	99.4%
Arsenic(as As)	0.3%
Cooper(as Cu)	0.01%
Iron(as Fe)	0.0002%
Lead(as Pb)	0.08%
Nickel(as Ni)	0.001%
Acidity(as H <sub>2</sub> SO <sub>4</sub> )	0.08%
Average particle size	1.25μm
Residue on 53 μm sieve (325 mesh)	0.005%

Ammonium Sulphate

(Siam Science Service Ltd.)

## **Apparatus**

### **1. Gas Chromatography**

Fisons model GC 8000 Series

### **2. Pyrolyzer**

Fischer Curie-Point pyrolysis model 0316M

### **3. Flammability Testing**

Flammability ( ISO 3795 )

Limit Oxygen Index ( LOI ASTM D 2803-91 )

Polymer Laboratories model FTA II

### **4. Tension Testing**

Tensile strength and elongation testing ( JIS K 6301 )

Tear strength testing ( JIS K 6301 )

Suga Universal Tester model AGS-500A

### **5. Two-Roll Mill**

Lab Tech Co., Ltd. model LRM 150

### **6. Mechanical Mixing Machine**

Lab Tech Co., Ltd. model LMX 5

## Sample Preparation

### 1. Blending PVC Ingredients

Blending is the first step in preparing a PVC compound for testing, the amount of ingredients required to blend can be calculated on part by weight of ingredient per 100 parts by weight of total PVC resin are employed.

A plasticized formulation can be blended at ambient temperature using a mixing procedure as follow:

a) Dissolve the lubricant in the plasticizer in a beaker by using gentle heating and agitation. Cool to room temperature and stir in any other liquid ingredients.

b) Add all solids (except the lubricant) to the mixing bowl.

c) Mix at slow speed for 1 minute.

d) Slowly add the plasticizer mix from step (a) to the bowl while continuing to mix at low speed.

e) Continue mixing for 1 minute after all the liquid from step (a) has been added.

f) Remove a portion of the mix from step (e) and use it to absorb the residual liquid from the beaker; add this back in the mixing bowl with the aid of a rubber spatula.

g) Scrape the sides of the mixing bowl and the mixing blade with a rubber spatula to be sure all ingredients are incorporated into the mix.

h) Mix at medium speed until a uniform mix is produced (typically 3-5 minutes).

## **2. Fluxing**

Fluxing is carried out typically on a two-roll mill. The material is placed on the mill and allowed to preheat for 1-2 minutes prior to start the roll turning. To aid mixing, the compound is cross cut back and forth using a mill knife. A batch should be mixed for a minimum of 5 minutes after banding. Distance between the rolls(the roll nip) is adjusted to facilitate fluxing. Later, the nip is adjusted for removal of the batch at 0.20 mm. thickness of test sheets.

## Recipes of Polyvinyl Chloride Compounding

The samples of polyvinyl chloride were prepared as follows

### Recipe 1 : Plasticized Polyvinyl Chloride ( no fire retardant )

**Table 3-3** Ingredient used in hard, soft and highly soft polyvinyl chloride film ( no fire retardant )

Ingredient	Formulation		
	Hard film	Soft film	Highly soft film
PVC K-60	100	-	-
PVC K-65	-	100	-
PVC K-70	-	-	100
Plasticizer	25	40	70
Co-stabilizer	2	2	2
Stabilizer	1	1	1
Lubricant	0.2	0.2	0.2
Filler	10	10	10

**Recipe 2 : Fire-retardance plasticized polyvinyl chloride film****Fire retardant used : Zinc hydroxy stannate (ZHS)****Table 3-4 Ingredient used in fire-retardance plasticized polyvinyl chloride film ( ZHS fire retardant )**

Ingredient	Formulation		
	Hard film	Soft film	Highly soft film
PVC K-60	100	-	-
PVC K-65	-	100	-
PVC K-70	-	-	100
Plasticizer	25	40	70
Co-stabilizer	2	2	2
Stabilizer	1	1	1
Lubricant	0.2	0.2	0.2
Filler	10	10	10
Fire retardant :			
ZHS 1 PHC	1.38	1.53	1.83
ZHS 2 PHC	2.76	3.06	3.66
ZHS 3 PHC	4.15	4.60	5.50
ZHS 4 PHC	5.53	6.13	7.33
ZHS 5 PHC	6.91	7.66	9.16
ZHS 10 PHC	13.82	15.32	18.32



**Recipe 3 : Fire-retardance plasticized polyvinyl chloride film****Fire retardant used : Zinc stannate (ZS)****Table 3-5 Ingredient used in fire-retardance plasticized polyvinyl chloride film ( ZS fire retardant )**

Ingredient	Formulation		
	Hard film	Soft film	Highly soft film
PVC K-60	100	-	-
PVC K-65	-	100	-
PVC K-70	-	-	100
Plasticizer	25	40	70
Co-stabilizer	2	2	2
Stabilizer	1	1	1
Lubricant	0.2	0.2	0.2
Filler	10	10	10
Fire retardant :			
ZS 1 PHC	1.38	1.53	1.83
ZS 2 PHC	2.76	3.06	3.66
ZS 3 PHC	4.15	4.60	5.50
ZS 4 PHC	5.53	6.13	7.33
ZS 5 PHC	6.91	7.66	9.16
ZS 10 PHC	13.82	15.32	18.32

**Recipe 4 : Fire-retardance plasticized polyvinyl chloride film****Fire retardant used : Antimony trioxide ( $\text{Sb}_2\text{O}_3$ )****Table 3-6 Ingredient used in fire-retardance plasticized polyvinyl chloride film (  $\text{Sb}_2\text{O}_3$  fire retardant )**

Ingredient	Formulation		
	Hard film	Soft film	Highly soft film
PVC K-60	100	-	-
PVC K-65	-	100	-
PVC K-70	-	-	100
Plasticizer	25	40	70
Co-stabilizer	2	2	2
Stabilizer	1	1	1
Lubricant	0.2	0.2	0.2
Filler	10	10	10
Fire retardant :			
$\text{Sb}_2\text{O}_3$ 1 PHC	1.38	1.53	1.83
$\text{Sb}_2\text{O}_3$ 2 PHC	2.76	3.06	3.66
$\text{Sb}_2\text{O}_3$ 3 PHC	4.15	4.60	5.50
$\text{Sb}_2\text{O}_3$ 4 PHC	5.53	6.13	7.33
$\text{Sb}_2\text{O}_3$ 5 PHC	6.91	7.66	9.16
$\text{Sb}_2\text{O}_3$ 10 PHC	13.82	15.32	18.32

**Recipe 5 : Fire-retardance plasticized polyvinyl chloride film****Fire retardant used : Ammonium sulphate (AS)****Table 3-7 Ingredient used in fire-retardance plasticized polyvinyl chloride film ( AS fire retardant )**

Ingredient	Formulation		
	Hard film	Soft film	Highly soft film
PVC K-60	100	-	-
PVC K-65	-	100	-
PVC K-70	-	-	100
Plasticizer	25	40	70
Co-stabilizer	2	2	2
Stabilizer	1	1	1
Lubricant	0.2	0.2	0.2
Filler	10	10	10
Fire retardant :			
AS 1 PHC	1.38	1.53	1.83
AS 2 PHC	2.76	3.06	3.66
AS 3 PHC	4.15	4.60	5.50
AS 4 PHC	5.53	6.13	7.33
AS 5 PHC	6.91	7.66	9.16
AS 10 PHC	13.82	15.32	18.32

## Measurement

### 1. Mechanical properties testing (9)

#### Tensile strength and elongation testing

Each of the five test pieces conforms to the dimension shown in Figure 3-1 were taken from the test specimen in the longitudinal and lateral directions and shall be provided on the center with two bench marks with a distance of 40 mm. The test piece then be mounted on a tension tester as shown in Figure 3-2 and pulled at a speed of 200 mm/min. with the distance between tester jaws set to 90 mm. When the tester indicates a maximum load, the load applied and the distance between the bench marks shall be obtained. The tensile strength was expressed by the load found in  $\text{kgf/cm}^2$  ( $\text{N/cm}^2$ ) when a maximum load was marked. The tensile strength and elongation at break were calculated from the following formula.

$$\text{Tensile strength} = F/A$$

Where, F = maximum load (Kgf)

A = cross-section area of test piece ( $\text{cm}^2$ )

$$\text{Elongation (\%)} = [(L-L_0)/L_0] \times 100$$

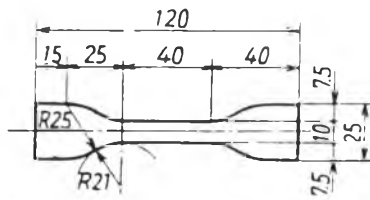
Where, L = distance between bench marks at the point of rupture (mm)

$L_0$  = original distance between bench marks

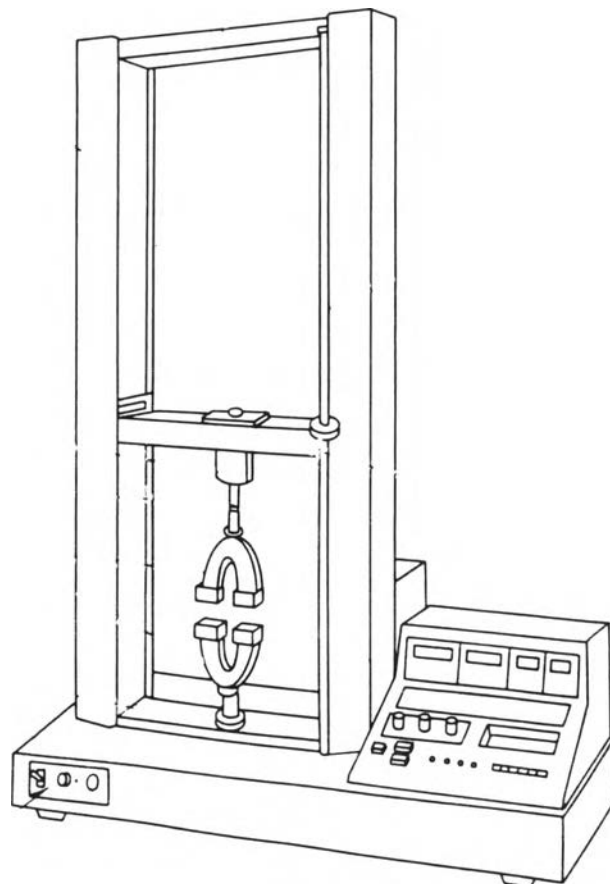
The test results were expressed in an average value of each five test piece taken in the longitudinal and lateral directions.

In the test piece is cut off at a point other than the area between the bench marks, the measured value shall not be employed and another test piece shall be prepared for retesting.

**Figure 3-1 Tension test specimen dimension**



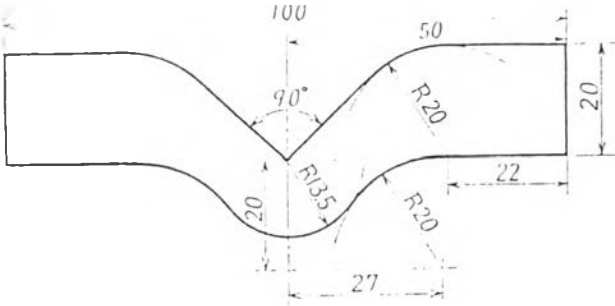
**Figure 3-2 Universal tester load frame, set up for tensile testing of plastics**



**Tearing Strength Testing**

Each five test pieces, dimension as shown in Figure 3-3, shall be taken in the longitudinal and lateral directions clamped by the tester jaws so that the test piece shall then be torn at a tension speed of 200 mm/min. The test result shall be expressed in an average value, by kgf(N), of each five test pieces in the longitudinal and lateral directions. When a constant speed elongation type tension tester with an automatic recorder is used, an average value of the maximum

**Figure 3-3 Dimension of tear test specimen**



## 2. Flammability Testing

### Flammability Testing (10)

For the purpose of this test, test specimens shall be conditioned by being left at a temperature of  $23 \pm 2^{\circ}\text{C}$  and at a relative humidity of  $50 \pm 5\%$  for a period not less than 24 hours and not more than 7 days. The tests were conducted in a metal box as shown in Figure 3-4 in a laboratory whose temperature and relative humidity are kept at said values.

The box was provided with an access window of a heat resistant glass plate in the front, and, a door that shall allow two U-shape metal plates (hereinafter referred to as U-shape Clamp) as shown in Figure 3-5 to enter the box, and a hole for passing a hose from a gas burner, on the side. The box also be provided with four slits 15 mm in width on the upper part of all sides and the bottom plate shall have ten gores 19 mm in diameter. The box was fitted with legs and the bottom part shall be raised by 10 mm.

A test piece 100 mm in width, 356 mm in length, and as shown in Figure 3-6 was chucked in the U-shape Clamp. Where the burning end of the test piece was softened and deflected, a 0.25 mm heat resistant wire was passed over the U-shape Clamp spaced at an interval of 25 mm to support the test piece.

The U-shape Clamp was held horizontal in the center of the box and a Bunsen Burner was placed that the center of the nozzle of the burner was positioned about 19 mm lower the center of the opening of the test piece. The Bunsen Burner was 9.5 mm in inside diameter and the total calorific value of the gas for testing shall be about  $9080 \text{ kcal/m}^3$  ( $38\text{MJ/m}^3$ ). The burner was held vertical and adjusted so as to generate a flame 38 mm in length and the air vent was kept closed.

(38MJ/m<sup>3</sup>). The burner shall be held vertical and adjusted so as to generate a flame 38 mm in length and the air vent shall be kept closed.

A flame shall be allowed to strike the test piece for 15 seconds and time from the time when the flame reaches the first measuring point to the time when the flame reaches the second measuring point shall be measured. The burning rate shall be calculated from the following formula. On starting the test the burning apparatus and U-shape Clamp shall be kept at a temperature of 30°C or lower.

$$\text{Burning rate (mm/min.)} = 60 \times (D/T)$$

Where: D = burning distance (mm)

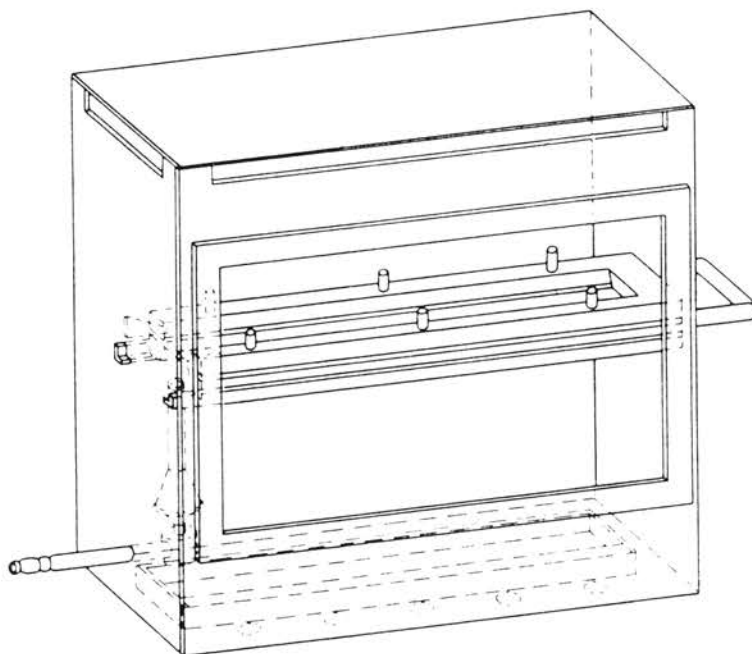
T = time required for burning over a distance of D mm (s)

The test shall be conducted under such conditions as to lead to the most disadvantageous results. If a flame goes out before reaching the second measuring point, hours required for the flame to go out shall be measured.

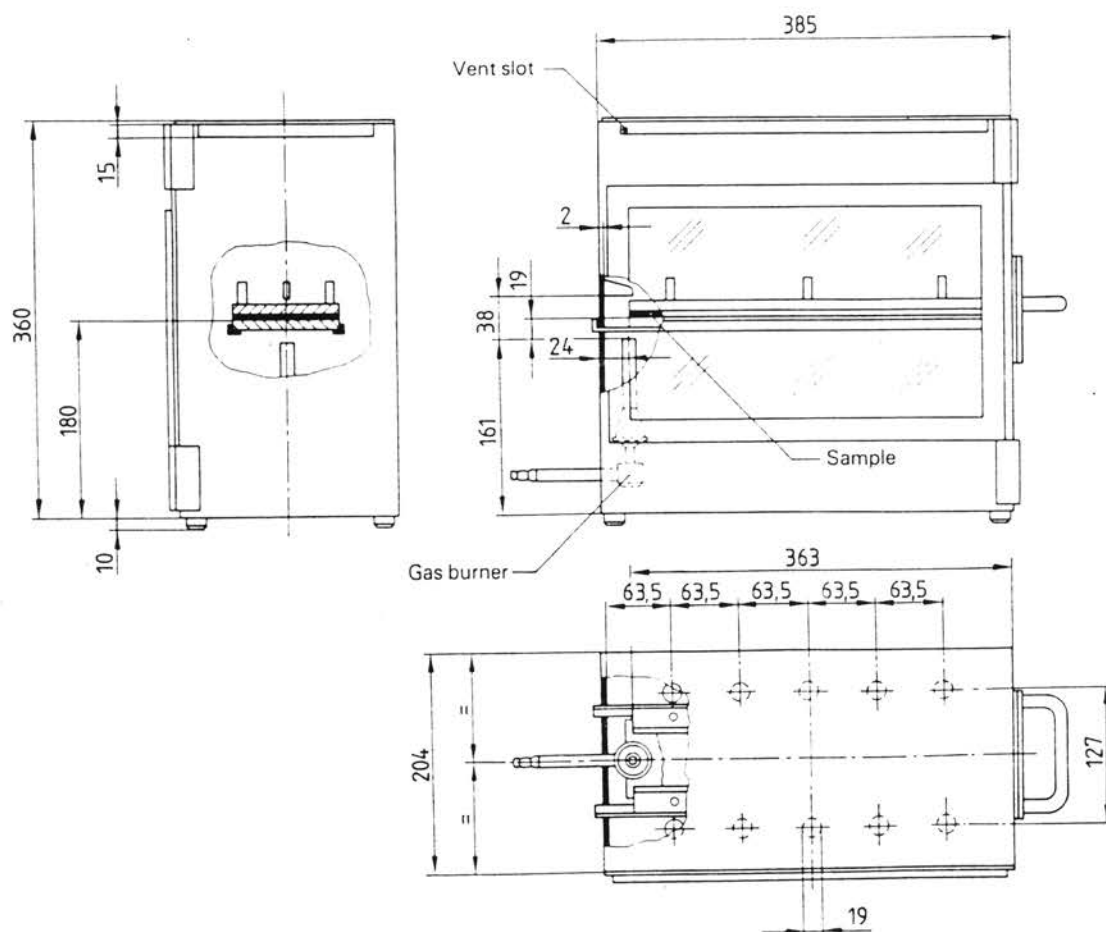
Even if a flame is started but if it does not reach the first measuring point, the burning rate shall be regarded as self-extinguished.



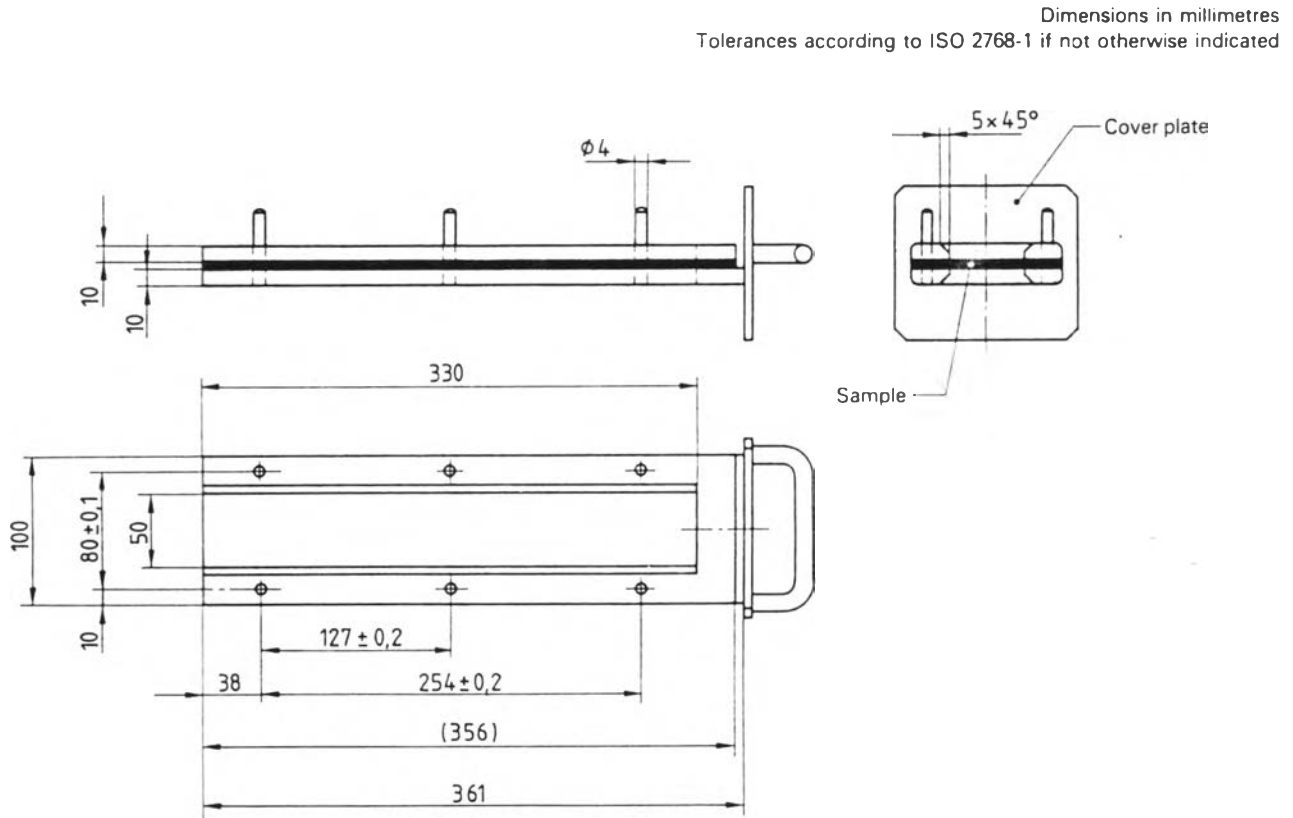
**Figure 3-4 Example of combustion chamber**



Dimensions in millimetres  
Tolerances according to ISO 2768-1

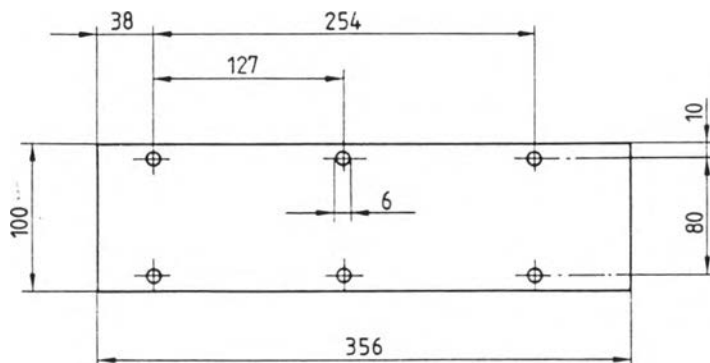


**Figure 3-5 Example of U-shape clamp**



**Figure 3-6 Test piece**

Dimensions in millimetres



### **Limit Oxygen Index (LOI)**

Oxygen index is defined as the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature under specified conditions. The oxygen test is considered one of the most useful flammability tests since it allows one to precisely rate the materials on a numerical basis and simplifies the selection of plastics in terms of flammability. The oxygen index tester is shown in Figure 3-7.

**Figure 3-7 Oxygen index tester**



Test procedures are as follows:

- a) Ensure oxygen and nitrogen are connected and turn on
- b) Connect mains to the instrument and switch the switch on the rear panel on. Leave to stabilize for 15 minutes.
- c) With O<sub>2</sub> on/off valve closed, open N<sub>2</sub> on/off valve. Adjust N<sub>2</sub> needle valve until the flowmeter indicates a flow of 18 l/min.
- d) Adjust zero potentiometer for a display of 0.00 %O<sub>2</sub>
- e) Close N<sub>2</sub> on/off valve and open O<sub>2</sub> on/off valve. Adjust O<sub>2</sub> needle valve until the flowmeter indicates a flow of 18 litres/minute.
- f) Adjust span potentiometer for a display of 99.7 %O<sub>2</sub> (or the %O<sub>2</sub> of the oxygen used).
- g) Close the O<sub>2</sub> on/off valve.
- h) Cut the sample to the required size, as indicated by appropriate standard and place in the sample holder.
- i) Remove chimney and place sample holder with loaded sample in position (see Figure 3-8).
- j) Place chimney over sample holder and sample, and ensure it is clipped securely into retaining clips.
- k) Light the burner and place in a safe position.
- l) Open both O<sub>2</sub> and N<sub>2</sub> on/off valves and adjust both needle valves until the total flow is 18 l/min. and the concentration of O<sub>2</sub> is as required for the sample. Purge at this flow rate for 30 to 40 seconds to ensure stability.  
  
(N.B. If the sample being tested is unknown, set the starting O<sub>2</sub> concentration to approximately 25% O<sub>2</sub>)
- m) Using the burner, light the sample following the precise protocol for the standard being followed.

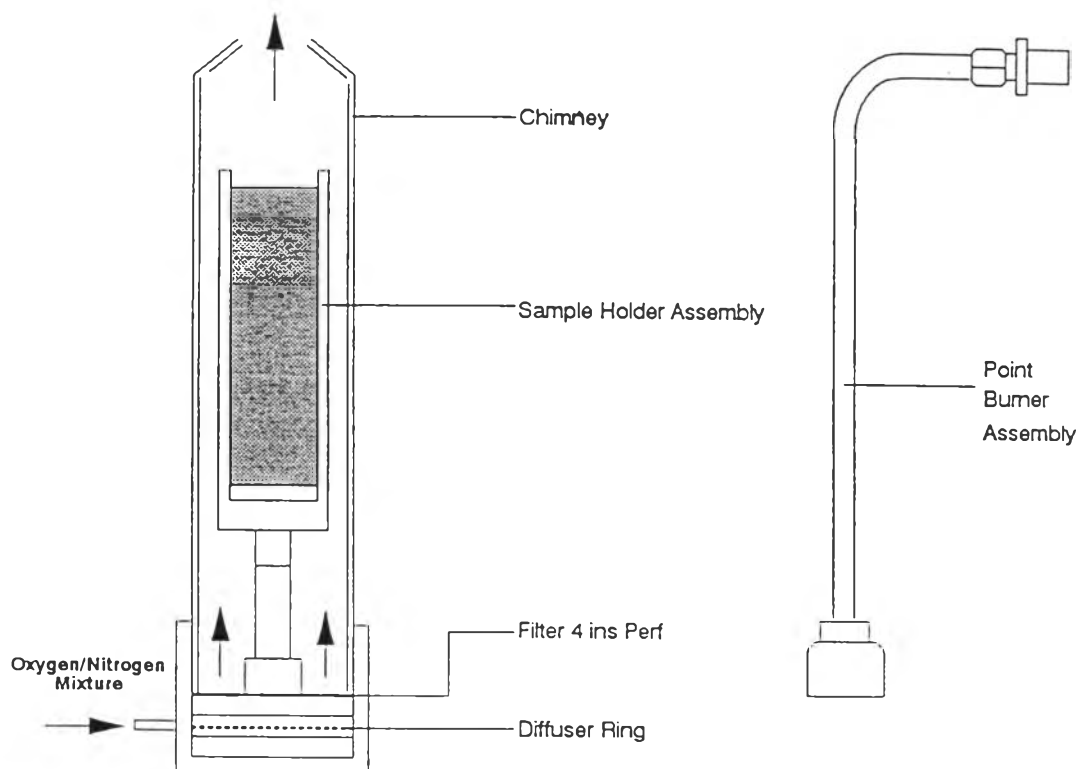
n) Using the  $O_2$  and  $N_2$  needle valves, adjust the  $O_2$  concentration, whilst maintaining the flow at 18 l/min., so that the sample burning front is just maintained.

o) Record the  $O_2$  concentration as the oxygen index percent.

p) At the completion of the run, close the  $O_2$  and  $N_2$  on/off valve and the needle valves. Remove the chimney and sample holder and any remnants of the sample.

q) Unless further runs are to follow, turn off the instrument and the  $O_2$  and  $N_2$  supplies.

**Figure 3-8 Chimney and burners**



### **3. Evolved Gas Analysis**

#### **Pyrolysis Gas Chromatography**

The pyrolysis, i.e. the decomposition into low-molecular compounds by high temperatures, has been applied since long for the analysis of organic polymers and copolymers. These low-molecular pyrolysis products are then analyzed according to usual procedures which show the chemical composition and structure of source material. This kind of analysis could be considerably facilitated by the combination of the pyrolysis with gas chromatography, mass spectrometry (MS) or the Fourier-Transform Infrared spectrometry (FTIR) and is now an important procedure for the analytical identification of the structural properties of high polymers and tensides.

#### **Curie-Point Pyrolysis**

The principle of the Curie-point Pyrolysis uses the property of a ferromagnetic filament to be shockheated to its Curie-temperature. In the center of a cylindrical induction coil, the filament is induced by a magnetic field with an adequate impulse frequency. When the Curie-temperature is reached, there is a drop of filament's relative permeability - its ferromagnetic status becomes paramagnetic, whereby the heating capacity which is taken up by the filament drops very quickly to an extremely low value.

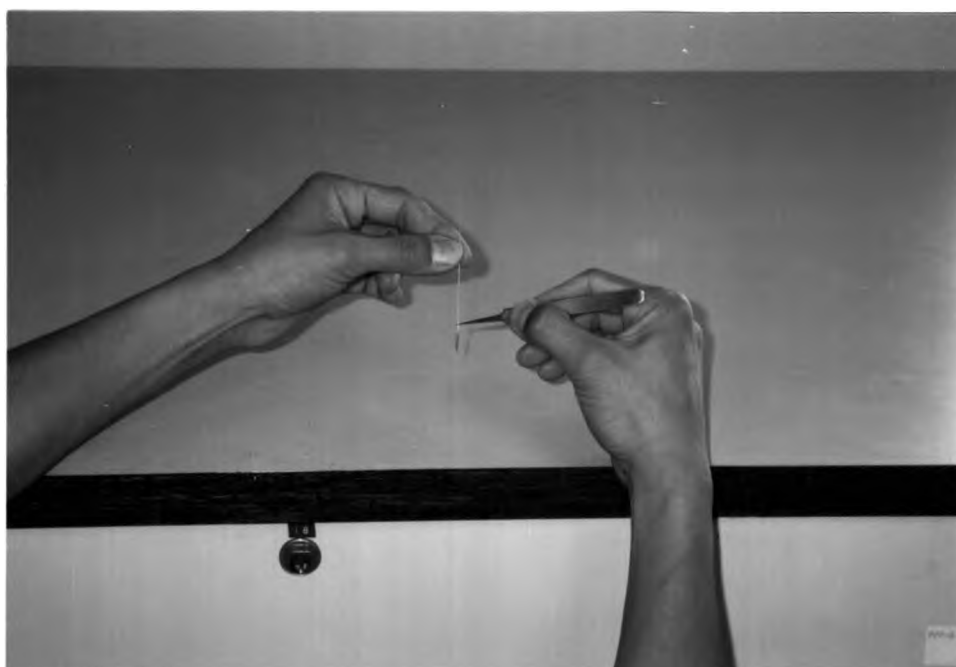
#### **Application of Samples**

Depending on the alloy composition of the ferromagnetic sample holder, the pyrolysis temperature between 300-1000<sup>o</sup>C can be achieved. In



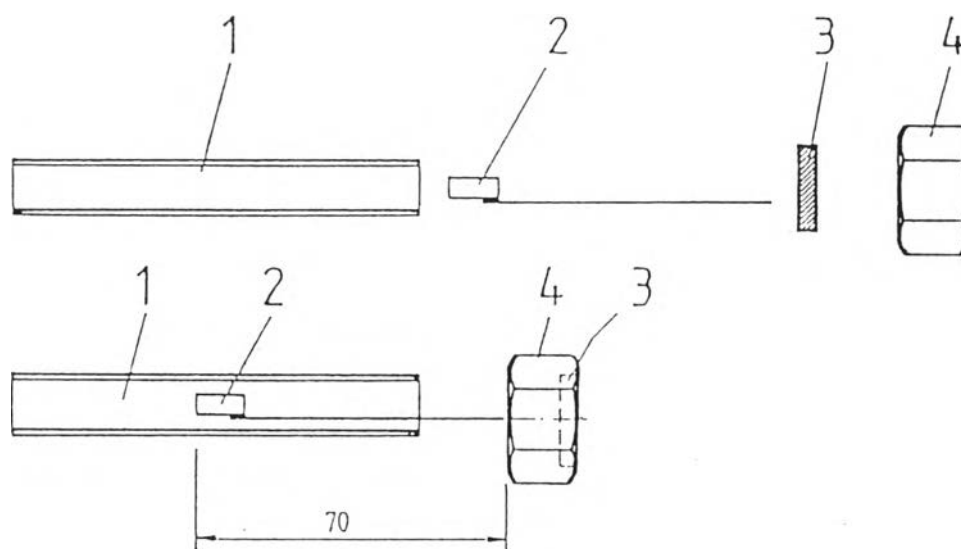
this work the samples were pyrolyzed for 9 second with the use of ferromagnetic tubes for  $700^{\circ}\text{C}$ . For the application of solid samples, spiral shape ferromagnetic sample holder are used. The solid sample is filled into the center of a ferromagnetic spiral by means of a forceps (see Figure 3-9)

**Figure 3-9 Application of solid sample and sample carrier**



The sample holder with screw socket (see Figure 3-10) is first push into the quartz tube and then insert into the pyrolysis chamber ( see Figure 3-11 ). The screw socket are screwed to the T-piece.

**Figure 3-10 Assembly of the sample holder with septum of screwing and quartz tube**



- |                  |                                |
|------------------|--------------------------------|
| 1 Quartz tube    | 2 ferromagnetic sample carrier |
| 3 Silicon septum | 4 Screw socket                 |

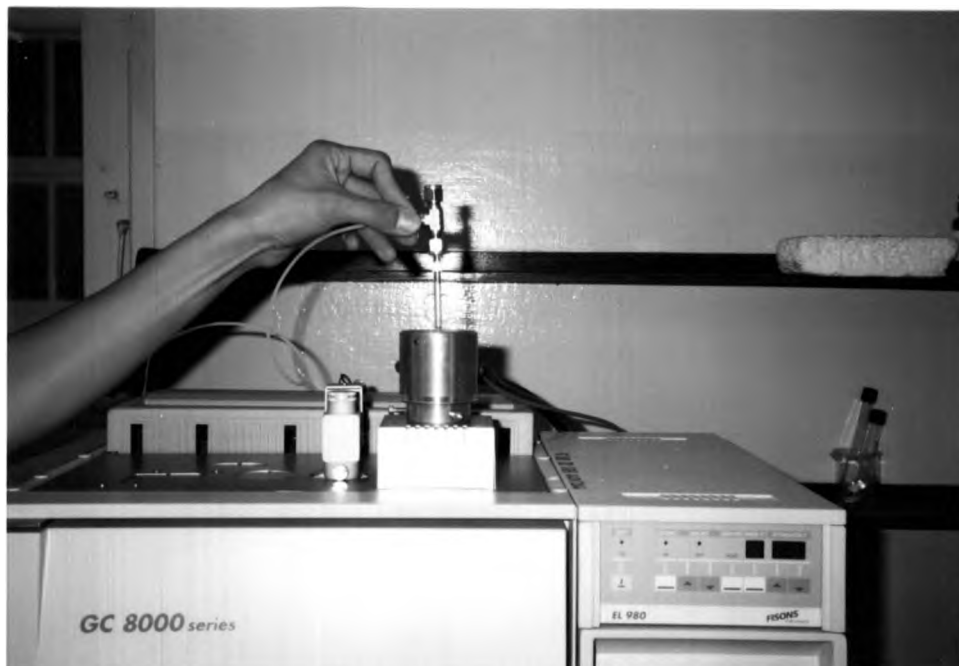
### Pyrolysis

The pyrolysis procedures are as follows.

- a) Adjust the pyrolysis time to 9 seconds.
- b) Adjust the temperature to 200°C at the temperature controller for additional heating of the reactor.
- c) Push the pyrolysis injector into the induction coil in such manner that the GC-septum is pierced by the injection needle. ( see Figure 3-11 )
- d) When the gas-chromatograph and the pyrolysis apparatus are ready for start, The pyrolysis is started with the start key and following by the starting of gas-chromatograph.
- e) After the GC-programme has been ended and the column has cooled down, the next sample can be started.



**Figure 3-11 Pyrolysis injector**



### **Gas Chromatography**

The gas-chromatograph analyses were performed by using an GC 8000Series chromatograph (Fision, Norwalk, Connecticut, U.S.A.) equipped with a flame-ionization detector and fused silica capillary columns: 30 meters length, 0.25 mm.i.d., stationary phase - OV-1701, film thickness 0.1-0.15 micron. The temperature of column was programmed from 50°C after 3 minutes to 220°C with an increment of 10°C/min. and then operated isothermally at 220°C for 10 minutes. Detector and Injector temperature was 250°C.

Helium for chromatography was used as the carrier gas at a flow rate of 20 cm<sup>3</sup>/min. The FID was supplied with 30 cm<sup>3</sup>/min. hydrogen and 300 cm<sup>3</sup>/min. air.