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# A Flammability test for Granular Synthetic Resins using a Modified Oxygen Index Method

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## Abstract

A new flammability test has been developed for granular synthetic resins, based on a modified Japanese Industrial Standard (JIS) oxygen index test. In addition, an oxygen index has been determined for several different materials using the newly proposed method. The Appropriateness of the new test method is examined by comparison to oxygen indexes as measured by the conventional test.

## 1. Introduction

Materials for which fire spreads rapidly, or which are difficult to extinguish, are classified in Japan as appointed flammable materials. Some synthetic resins fall into this category. In many cases these synthetic resins are stored and handled in the form of beads, granules, pastes, etc.

The oxygen index method <sup>1)</sup>, a prescribed Japanese Industrial Standard, is usually used as the flammability test method for synthetic resins. However, this test has been devised for sample in the form of sticks or textiles. It is therefore difficult to assess the flammability of synthetic resins in granular form using this standard oxygen index method. In addition, there are problems when applying the test to materials whose chemical composition is changed on heating, like thermosetting resins, or for materials which melt by slight heating, such as reactivity resins.

Tewarson et al. <sup>2,3)</sup> studied the flammability of polymeric materials using apparatus equipped with an external radiant heat panel, similar to that found in oxygen index testing equipment. This equipment has some advantages, because it can be used for granular polymer and measure the flammability of polymeric materials exposed to fire. However, the equipment is not in wide use, being confined to research studies.

In contrast, experimental studies of oxygen indexes has been regularly performed using existing oxygen index flammability test equipment <sup>4,5)</sup>. However, the oxygen index has been determined for film, textile and stick forms, and as far as the authors are aware, the oxygen index has not been measured for samples in granular form.

The prime purpose of this research has been to improve the oxygen index method when used to evaluate the flammability of granular synthetic resins. Moreover, a range of synthetic resin samples in stick or membranes forms were

fabricated and the new test method applied to allow comparison to oxygen index values as measured by the conventional oxygen index test.

## 2. Experiment

### 2.1 Test equipment

The equipment (ON-1 type) which was used to measure oxygen index is equivalent to the equipment stipulated in JIS K 7201. Reproducibility of results was confirmed by testing the material PMMA (Polymethylmethacrylate), which has a definite oxygen index value.

### 2.2 Sample holder

A sample holder made of stainless steel was fabricated to support granular polymer samples within the burning tube of the oxygen index equipment, shown in figure 1. This supporting implement was used instead of the existing sample holder for stick and textile, while also allowing granular sample to be tested.

### 2.3 Sample cap

A cap of quartz was made to contain the granular samples and the influence on oxygen index versus the size of the cap was examined. Caps diameter were 10,15,20 and 25 mm respectively, thickness is 1mm, height is 5 mm.

### 2.4 Ceramic paper

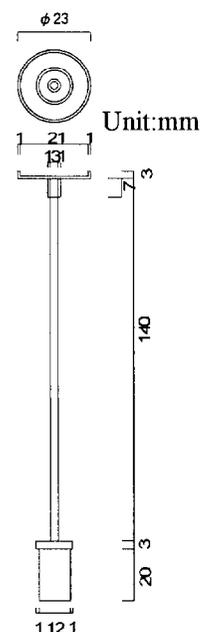
Ceramic paper of thickness 1mm was placed on sample support between the sample support and the sample cap. The heat loss from the sample was thereby reduced as much as possible. Ceramic paper used had the following properties;  $0.15\text{g/cm}^3$  for density,  $1260^\circ\text{C}$  for the highest used temperature, and  $0.06\text{ kcal/mh}^\circ\text{C}$  ( $400^\circ\text{C}$ ),  $0.08\text{ kcal/mh}^\circ\text{C}$  ( $600^\circ\text{C}$ ),  $0.10\text{ kcal/mh}^\circ\text{C}$  ( $800^\circ\text{C}$ ) and  $0.13\text{ kcal/mh}^\circ\text{C}$  ( $1000^\circ\text{C}$ ) respectively for heat conductivity.

### 2.5 Ignition source

Urban gas was used as an ignition source for the sample and the flame length was adjusted to be 20~30mm. The flame contact time was varied for each sample, and the flame was allowed to contact the sample until it was ignited. To ensure reproducibility of this flame contact condition, the distance between the burner front and the edge of the sample cap was essentially fixed.

### 2.6 Samples

27 different of samples were used; liquid paraffin, aromatic hydrocarbon resin, polyethylene (4 types of granule and 1 type of film), polypropylene (2 types of granule), polystyrene (3 types of granule), polyvinyl chloride (3 types of granule, 1 type of powder, 3 types of stick), polycarbonate, polyamide,



polybutylene terephthalate, polymethyl methacrylate, ABS resin, polyvinylidene fluoride and fluorocarbon resin (2 types). All the samples, except liquid paraffin and polyvinyl chloride (powder), are raw materials which have actually appeared in the market. In addition, 20 pieces of sample grain were picked out randomly and the maximum diameter was measured using a micrometer. Grain diameters shown in table 1 are the average of 20 values.

Sample no. 1, liquid paraffin, was used to examine the necessary size of the cap for testing thermoplastic materials.

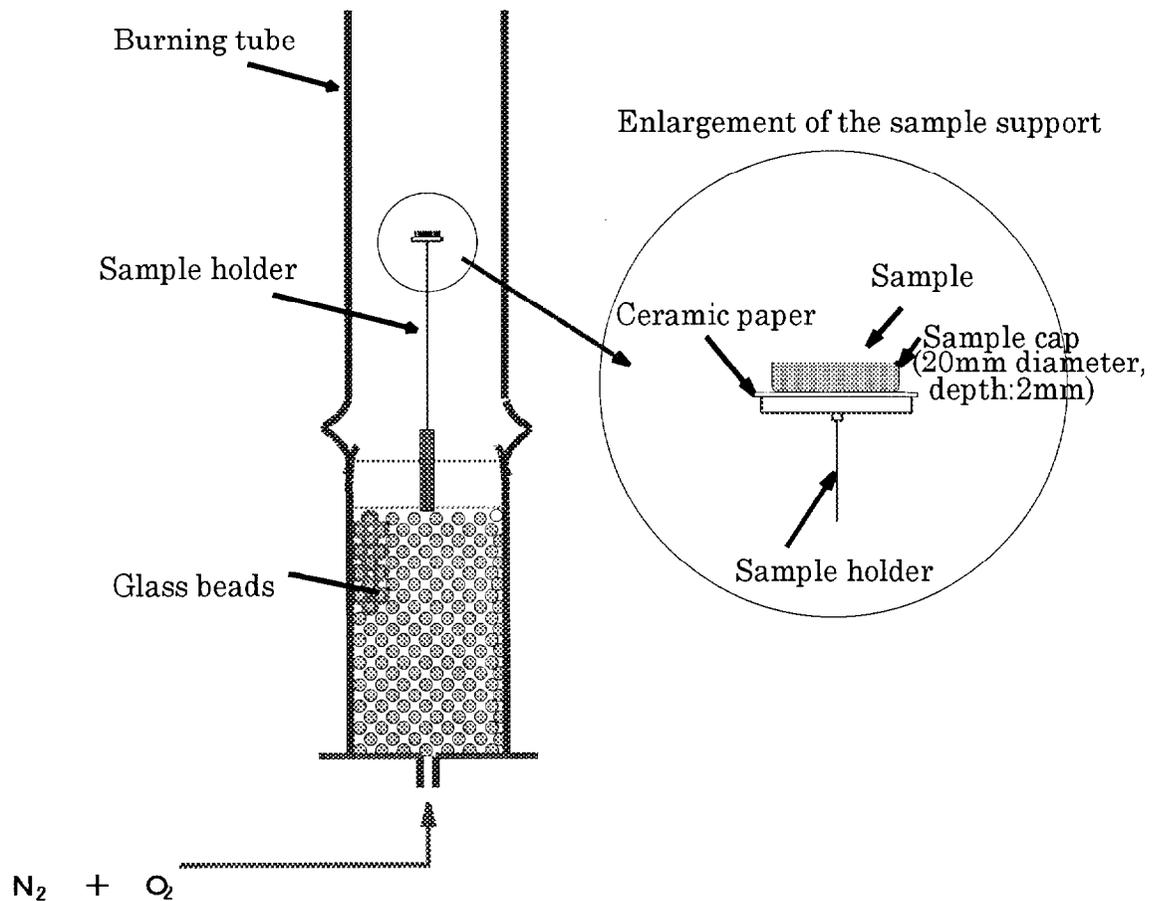
## 2.7 Test procedure

### (1) Method for supporting the samples

Each sample was packed level to the top surface of the sample cap and placed on the sample holder. Ceramic paper was laid between the sample holder and sample cap, to minimize heat loss. By using this method, the support of the samples could be united without having to consider the thermal properties of the samples. An outline of the sample support method is shown in figure 2.

### (2) Experimental method and measurement of the oxygen index

- 1) Sample is put into a quartz sample cap filled level to the top surface of the cap, and the sample weight is measured.



**Fig.2 Method for supporting granular samples**

- 2) A circular ceramic paper, 25mm in diameter, was placed on the sample holder, and the cap and sample weighed in 1), placed at its center.
- 3) The sample is located in the oxygen index apparatus and the oxygen atmosphere in the burning tube is adjusted for the test.
- 4) The sample is ignited by a burner.
- 5) A residual weight after burning is measured, and the burn-up fraction is calculated using the following expression.

$$\text{Burn - up fraction} = \frac{\text{sample weight} - \text{residual weight}}{\text{sample weight}} \times 100$$

- 6) Change the oxygen concentration in intervals of about 1% between the start point when burn-up fraction is increasing, and the end point when it attains roughly a fixed value: The operational procedure from 1) to 5) is repeated.
- 7) A maximum burn-up fraction is determined and the conversion burn-up fraction is calculated from the following expression.

$$\text{Conversion burn - up fraction} = \frac{\text{burn - up fraction}}{\text{maximum burn - up fraction}} \times 100$$

- 8) The conversion burn-up fraction is plotted against oxygen concentration and an S-type curve fitted to the data. The conversion burn-up fraction at 50% is taken as the oxygen index of the sample.

In addition, a stick and film samples were tested following the method prescribed in JIS K 7201.

Furthermore, burning behavior was recorded on video and photographs were taken during the tests.

The method to determine the oxygen index is shown graphically in figure 3.

### 3. Results

It can be expected that the relation between oxygen concentration and burn-up fraction will be an S-type curve. This is based on the assumption that the curve is a logistic curve.

The Results for oxygen index as measured by the new method are shown in table 1. Oxygen index values determined by fitting an S-type curve to the relation between oxygen concentration and conversion burn-up fraction are compared to oxygen index values from the literature.

The following text explains how cap size was determined by using liquid paraffin, discusses the burning behavior of each sample, and compares oxygen indexes measured by the new method proposed here to indexes measured by the conventional technique.

#### 3.1 Liquid paraffin

Using liquid paraffin as sample No. 1, the influence on oxygen index of the size of the quartz cap was investigated. The results are shown in figure 4. The oxygen index was also determined by the conventional method.

Table 1 Oxygen index for granular synthetic resins

Sample No.	Sample name	Configuration	Diameter (mm)	Oxygen index (1)	Oxygen index (2)	Reference <sup>7,8)</sup>
1	Liquid paraffin	Liquid	—	16.7	16.7	—
2	Aromatic hydrocarbon resin	Granular	5.5	19.8	19.8	—
3	Polyethylene A	Granular	3.6	20.2	20.3	18.8~19.3
4	Polyethylene A	Film	—	21.3	—	
5	Polyethylene B	Granular	3.6	18.6	18.2	
6	Polyethylene C	Granular	3.8	19.4	19.3	
7	Polyethylene D	Granular	4.0	18.9	18.8	
8	Polypropylene A	Granular	4.0	18.3	18.2	19.0
9	Polypropylene B	Granular	3.9	19.2	19.1	18.1
1 0	Polystyrene A	Granular	3.3	20.8	20.7	
1 1	Polystyrene B	Granular	2.9	23.4	23.4	
1 2	Polystyrene C	Granular	2.9	21.6	21.7	18.6~18.8
1 3	Polymethyl methacrylate	Granular	3.2	18.6	18.3	
1 4	Polyamide	Granular	2.5	24.3	24.3	24
1 5	Polybutylene terephthalate	Granular	3.4	24.5	24.3	—
1 6	ABS resin	Granular	2.7	19.6	19.4	19~20
1 7	Polycarbonate	Granular	3.0	31.2	31.8	26~28
1 8	Polyvinyl chloride A	Granular	3.3	39.5	39.4	45~49
1 9	Polyvinyl chloride A	Stick	—	33.0	—	
2 0	Polyvinyl chloride B	Granular	2.9	39.2	39.1	
2 1	Polyvinyl chloride B	Stick	—	32.2	—	
2 2	Polyvinyl chloride C	Granular	3.2	38.5	39.7	
2 3	Polyvinyl chloride C	Stick	—	34.0	—	
2 4	Polyvinyl chloride D	Powder	—	40.8	43.7	
2 5	Polyvinylidene fluoride	Granular	3.5	58.0	56.1	—
2 6	Fluorocarbon resin A	Granular	3.6	> 90	> 90	95.0
2 7	Fluorocarbon resin B	Granular	3.2	> 90	> 90	

Oxygen Index (1) : Values determined by fitting an S-type curve to the relation between oxygen concentration and conversion burn-up fraction as a rough estimate.

Oxygen Index(2) : Values determined by fitting a logistic curve to this relation using a least squares method.

Each point in figure 4 is the average value of the oxygen index measured 3 separate times. This figure indicates that when the diameter of the quartz cap is small, the heat loss is large and oxygen index increases. When the cap size is 20mm, the oxygen index is approximately constant. It was therefore concluded that it is suitable to use a quartz cap of 20mm diameter.

The influence of depth of the cap was not checked. For deeper caps, the sample quantity increases, and the flame-contact time is longer.

Based on the above, the oxygen index of the remaining samples was measured using a quartz cap of 20mm diameter, depth 2mm.

### 3.2 Aromatic hydrocarbon resin

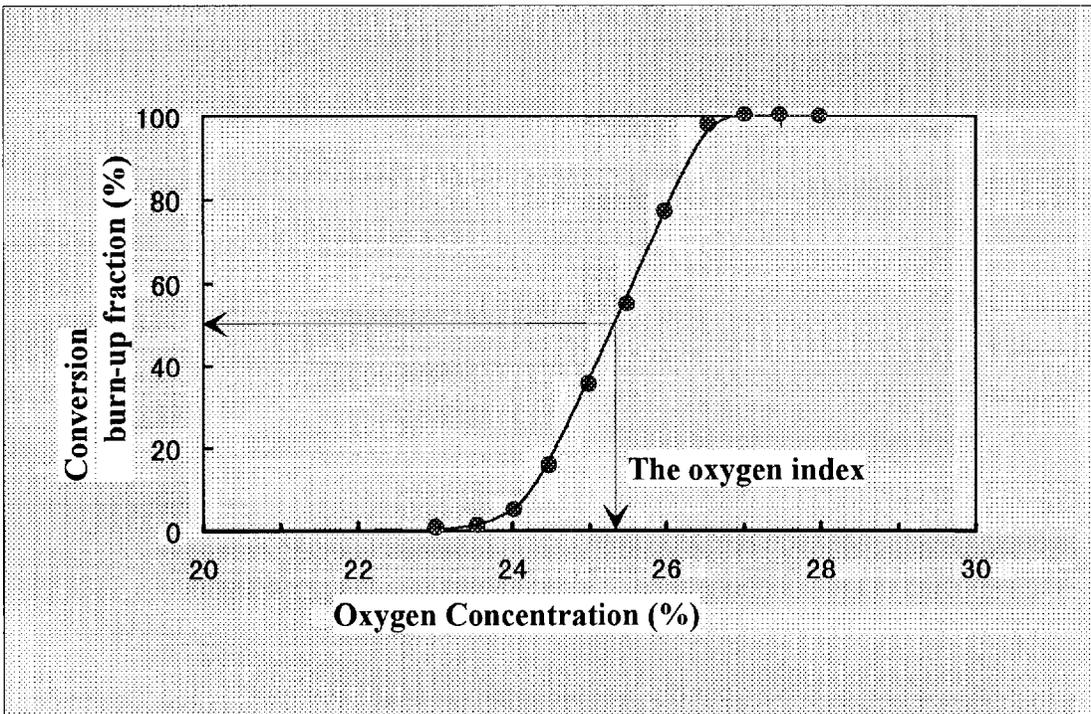
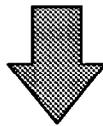
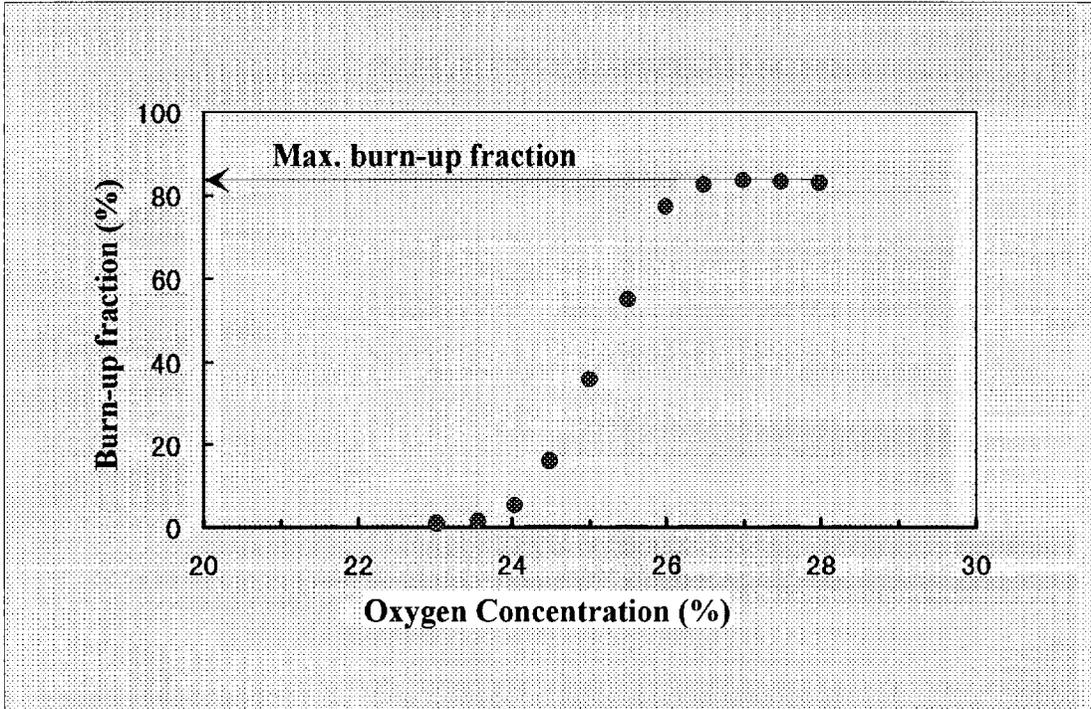
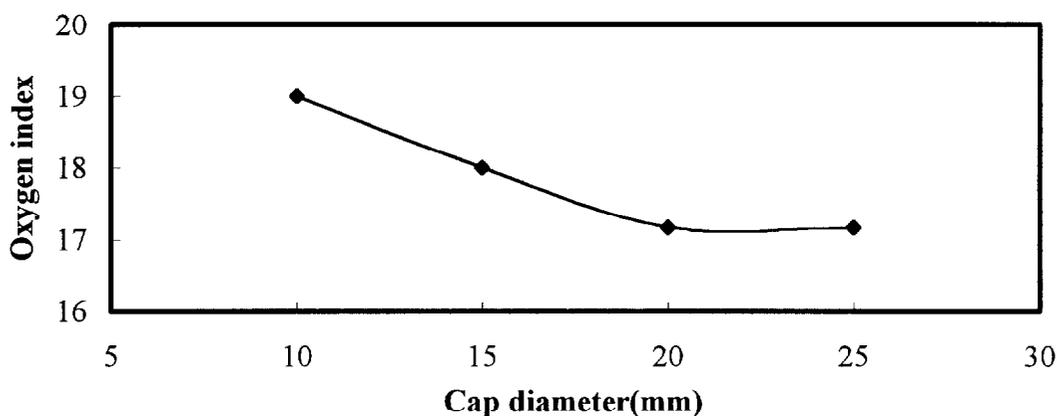


Fig 3 Determination of the oxygen index



**Fig.4 The effect of cap diameter on the oxygen index**

Polymerizing resins of materials such as indene, vinyltoluene and the present sample are used as the raw materials such as paints, rubber combination agents, printing ink, an adhesives. The melting point of this resin is low, and it changed readily into the liquid state when a pilot flame was placed in contact with the sample.

After melting entirely, on contact with the pilot flame, it ignited. In some cases the sample took about 5 minutes to form a stable flame on contact with the pilot flame. The flame had a yellow luminosity and generated soot from its tip. Burning behavior near the oxygen index is shown in figure 5 (b). The oxygen index value was 19.8.

### 3.3 Polyethylene

5 types of polyethylene No. 3~7 were prepared as samples. No.4 is the only film-shaped sample, the others were all granular samples. No.5 is a high-density polyethylene from a different manufacture to that of No.3 and No.4. No.6 is a low-density polyethylene. No.7 is different again from the above-mentioned polyethylenes.

Granular samples melted on contact with the pilot flame and changed into a liquid state. The time from flame contact to the formation of a stable flame, that is, the flame-contact time, was the same as for the aromatic hydrocarbon resin above. The flame had little yellow luminosity, but was pale and nearly transparent. Burning behavior near the oxygen index for sample No. 3 is shown in figure 5 (c).

Oxygen indexes of samples No.3 ~ 7 were found to be 20.2, 21.3, 18.6, 19.4, and 18.9, respectively. When the oxygen index of No. 3 was compared with that of No.4, the value of No.4 (film-shaped sample) was about 1 point higher than that of No.3. This may well be due to its different form. The oxygen index of No.3 was slightly higher than the literature value of polyethylene; 18.8~19.3<sup>7)</sup>. The others were the same as the literature values.

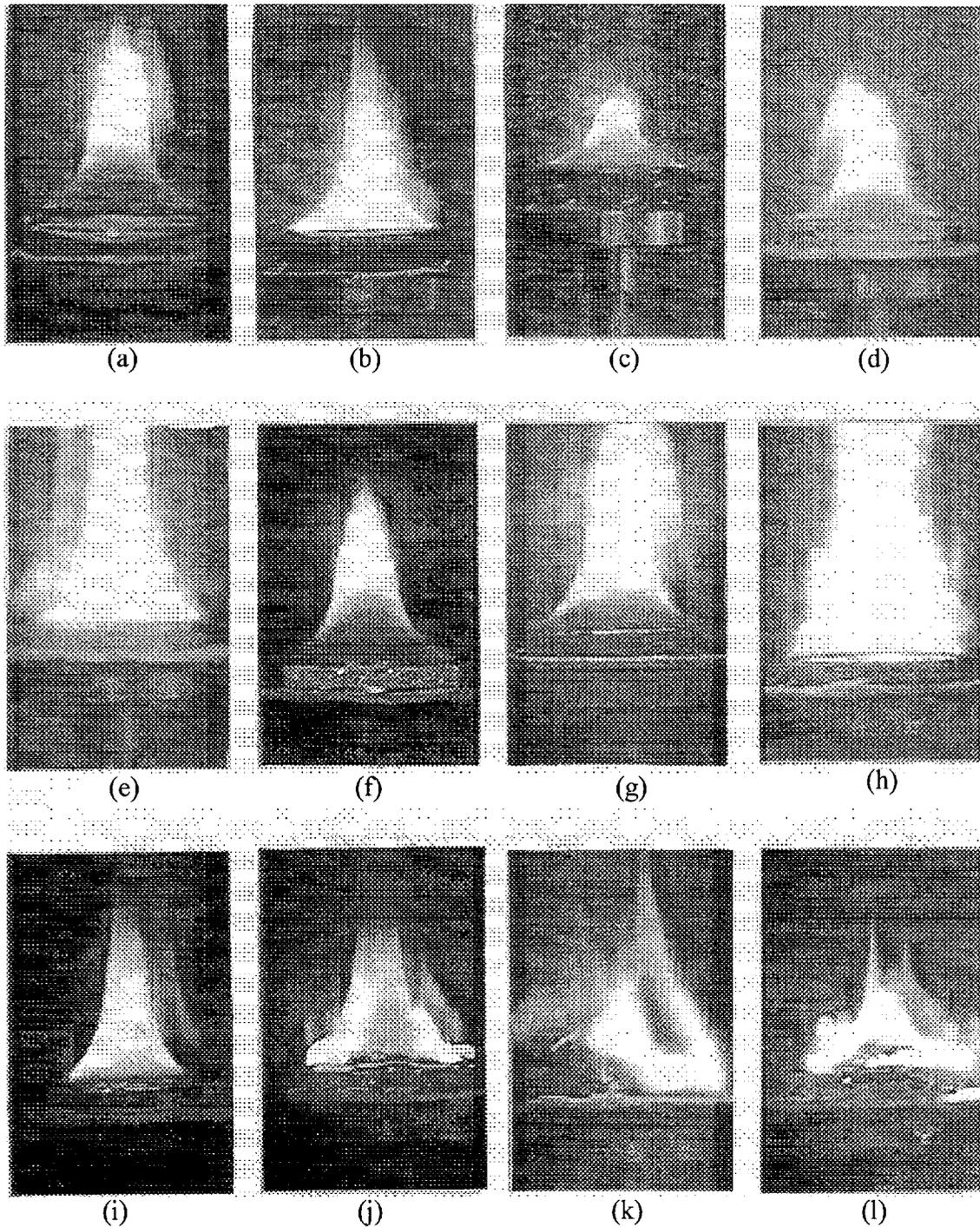


Figure 5 Burning behavior near the oxygen index for granular synthetic resins.

- (a) Liquid paraffin (b) Aromatic hydrocarbon resin (c) Polyethylene
- (d) Polypropylene (e) Polystyrene (f) Polymethyl methacrylate
- (g) Polyamide (h) Polybutylene terephthalate (i) ABS resin
- (j) Polycarbonate (k) Polyvinyl chloride (l) Polyvinylidene fluoride

### 3.4 Polypropylene

2 types of Polypropylene, No.8 and No.9, were prepared as samples. These samples melted on contact with the pilot flame and changed into a liquid state in the same way as the polyethylene. The flame-contact time and the burning behavior were also similar to polyethylene. Burning behavior near the oxygen index for sample No. 8 is shown in figure 5 (d).

The oxygen indexes of samples No. 8 and No. 9 were 18.3, and 19.2, respectively. The oxygen index values were the same as the literature values.

### 3.5 Polystyrene

3 types of Polystyrene, including a styrene monomer about 400ppm ~ 650ppm as an impurity, were prepared as samples. The ignition behavior of polystyrene differed from that of the polyethylene. It ignited easily, before melting on contact with the pilot flame. The flame had a yellow luminosity and produced soot in large quantities. Burning behavior near the oxygen index for sample No.10 is shown in figure 5 (e).

Oxygen indexes of samples No. 10, No.11 and No.12 were 20.8, 23.4, and 21.6, respectively. There are about 3~5 points higher than the literature values.

### 3.6 Polymethyl methacrylate

1 type of sample No. 13 was prepared. Ignition behavior was similar to that of polystyrene. That is, before it had entirely melted on contacting with the pilot flame, it readily ignited. Ignition time was within 3 minutes. Burning behavior near the oxygen index for sample No. 13 is shown in figure 5 (f).

The oxygen index of sample No.13 was measured as 18.6. It was almost the same as the literature value, 18.6~18.8<sup>8)</sup>.

### 3.7 Polyamide

1 type of sample No.14 was prepared. Ignition behavior was like that of polyethylene. After it had entirely melted on contact with the pilot flame, it ignited. The flame had a yellow luminosity and produced soot. Burning behavior near the oxygen index for sample No.14 is shown in figure 5 (g).

The oxygen index of sample No.14 was measured as 24.3. It was almost the same as the literature value, 24.0<sup>8)</sup>.

### 3.8 Polybutylene terephthalate

1 type of sample No.15 was prepared. Ignition behavior was like that of polyethylene. After it had entirely melted on contact with the pilot flame, it ignited. The flame had a yellow luminosity and produced soot. Burning behavior near the oxygen index for sample No. 15 is shown in figure 5 (h).

The oxygen index of sample No.15 was measured as 24.5.

### 3.9 ABS resin

1 type of sample No.16 was prepared. Ignition behavior was similar to that of polystyrene. Before it had melted perfectly on contact with the pilot flame, it readily ignited. The flame had a yellow luminosity and produced soot in large

quantities. Burning behavior near the oxygen index for sample No.16 is shown in figure 5 (i).

The oxygen index of No.16 was measured as 19.6. It was almost the same as the literature value, 19~20<sup>8)</sup>.

### 3.10 Polycarbonate

1 type of sample, No.17 was prepared. It ignited easily on contact with the pilot flame. After the sample had burned, a carbonized residue was generated on the surface of the sample. Burning behavior near the oxygen index for sample No.17 is shown in figure 5 (j).

The oxygen index of No.17 was measured as 31.2. It was about 3 ~ 5 points higher than the literature value, 26~28<sup>7)</sup>.

### 3.11 Polyvinyl chloride

6 types of sample No. 18~23 were prepared. No.18, No.20, and No.22 are granular samples. No. 19, No.21 and No.23 are stick-shaped samples. Moreover, No. 18 and No.19, No. 20 and No.21, and No. 22 and No.23 are the same materials, respectively.

They ignited easily on contact with the pilot flame. The flame emitted a white flash and generated a carbonized residue. Burning behavior near the oxygen index for sample No.18 is shown in figure 5 (k).

The oxygen indexes of samples No.18 , No.19, No.20, No.21, No.22 and No.23 were measured as 39.5, 33.0, 39.2, 32.2, 38.5, 34.0, respectively. When the oxygen index of granular samples were compared with the values of stick-shaped sample for the same material, it was found to be about 4.5~7 points higher. This is mainly caused by the different forms. After the sample had burnt, a carbonized residue was generated within the cup. Further burning was prevented by the carbonized residue. When tested in a stick-shaped form, carbonized residue is generated, but, this does not prevent the sample from burning further. For samples generating a carbonized residue, as measured using the proposed oxygen index method, the oxygen index of granular sample can be expected to be higher than the values of stick-shaped samples. This is a characteristic of granular carbonized synthetic resins and is considered to be an essential flammability property of these resins.

### 3.12 Polyvinylidene fluoride

1 type of sample No. 25 was prepared. It ignited easily, in the same way as polyvinyl chloride on contact with the pilot flame. The flame had a yellow luminosity and generated a carbonized residue on the sample surface. Burning behavior near the oxygen index for sample No.25 is shown in figure 5 (l).

The oxygen index of No.25 was measured as 58.0.

### 3.13 Fluorocarbon resin

2 types of sample No. 26 and No.27 were prepared. Though they were tested in the largest oxygen concentration of the equipment, 90%, they merely evaporated and did not ignite. Measurement of an oxygen index was therefore not

possible for these samples. The oxygen index of fluorocarbon resin was 95.0 from the literature<sup>7)</sup>.

#### 4. Discussion

##### 4.1 Fitting the S-type curve

This relation is concerned with the oxygen index (1) as determined by fitting an S-type curve to the relation between oxygen concentration and conversion burn-up fraction, as a rough estimate, and oxygen index (2) determined by fitting a logistic curve to these relations using a least squares method. The logistic curve is given by the following equation.

$$Y = \frac{100}{1 + \exp[-b(X - a)]}$$

Where a and b are calculated by the least squares method, Y is the conversion burn-up fraction and X is oxygen concentration.

Oxygen index (2) was compared with oxygen index (1). The relation between these oxygen index values is shown in figure 6. The dotted straight line in the figure shows the relation between oxygen index (1) and oxygen index (2) to be 1:1. These data almost lies on this straight line. Therefore, it is concerned that the method for determining oxygen index by fitting an S-type curve as a rough estimate, is sufficient for practical purpose. Naturally there will be a difference between operators of the test, so in order to reduce scatter we must take care of the following.

- 1) When conversion burn-up fraction changes rapidly, the oxygen concentration must be altered slowly.
- 2) Samples with large scatter in oxygen index must be tested 3~5 times with identical oxygen concentrations.

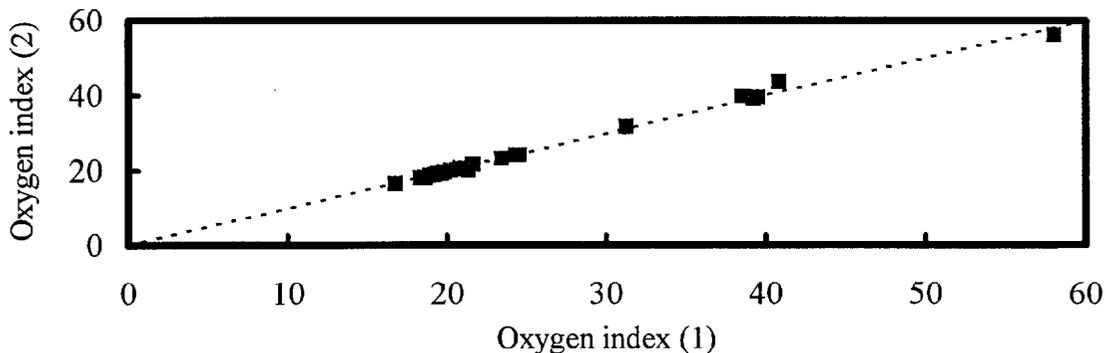


Fig.6 Relation between oxygen index determined by fitting an S-type curve, as a rough estimate, and fitting a logistic curve using the least squares method.

##### 4.2 Classification by heat property of the resin

The samples mentioned in this paper can be classified into three groups by their heat properties on contact with the pilot flame. Aromatic hydrocarbon resin, polyethylene, polypropylene, polyamide and polybutylene terephthalate fall into

the first group. These begin to ignite after entirely melting on contact with the pilot flame. Their oxygen index values were nearly the same as the literature values. This is because their burning behaviors is similar to that of stick samples tested using the conventional oxygen index method.

Polymethyl methacrylate, polystyrene and ABS resin fall into the second group. These materials are readily ignited before entirely melting. Their oxygen index values were almost the same as the literature values or slightly higher. It appears that they burn without losing granular form.

Polyvinyl chloride, polycarbonate and polyvinylidene fluoride fall into the third group. These materials are ignited also readily on contact with the pilot flame and generate a the carbonized residue on the sample surface. Their oxygen index values were considerably higher than the literature values. This is caused by the covering of the sample surface by the carbonized residue, considered to reflect the flammability property of these granular carbonized synthetic resins.

## 5. Conclusion

The conventional oxygen index method was modified for testing granular samples. 27 types of granular resin were tested using this modified test method. The result are as follows:

- 1) Oxygen index values of melting granular samples, such as polyethylene, are almost the same as those of their stick sample.
- 2) Oxygen index values of the easily ignitable and melting granular samples, such as polymethyl methacrylate, are almost the same as, or slightly higher, than those of their stick sample.
- 3) Oxygen index values of carbonizing granular samples, such as polyvinyl chloride, are considerably higher than those of their stick sample.

## 6. Reference

- 1) JIS K 7201, Testing Method for Flammability of Polymeric Materials Using the Oxygen Index Method , (1976) (in Japanese)
- 2) A.Tewarson and R.F.Pion, Flammability of Plastics - 1. Burning Intensity, COMBUSTION AND FLAME, 26, p.85(1976)
- 3) A.Tewarson, Heat Release Rate in Fires, FIRE AND MATERIALS, Vol.4, No.4, p.185(1980)
- 4) J.L.Isaacs, The Oxygen Index Flammability Test, J. FIRE & FLAMMABILITY, Vol.1, p.36, (1976)
- 5) L.Cegielka MA, The Burning Behaviour of Textiles and its Assessment by Oxygen-index Methods, Textile Volume 18 Number 1/2/3 , The Textile Institute, (1989)
- 6) The Catalogue KAOWOOL ACE-PAPER, Isoraito Ltd. (in Japanese)
- 7) Flammability Handbook for Plastics : CARLOS J. Hilado , TECHNOMIC, p.40(1969)
- 8) Plastic Data Handbook edited by K. Itou , Kougyoutyousakai,p.111(1980) (in Japanese)

## ***Discussion***

James Quintiere: Could you comment on the character of the flame, particularly on the Cone flame. Was it turbulence or laminar?

Eiji Yanai: Laminar.

Richard Lyon: Do I understand that you're determining not the oxygen concentration when the flame goes out, but a 50% weight loss concentration. What is the basis for that assumption?

Eiji Yanai: The definition of oxygen index is the boundary between whether it burns or it does not. If you look at a granular substance, which is not an ordinary sample for determining the oxygen index, we thought it was appropriate to get a 50% loss of weight.

Richard Lyon: So do you notice that the sample stops burning when it reaches a 50% weight loss peak? Did you notice that it didn't burn at that point and that was the reason for picking that particular criteria?

Eiji Yanai: Are you asking whether we took into consideration that when we ignited, it was burned already?

Richard Lyon: No. Was the point at which the sample would no longer sustain burning, was that equal to the time point at which the weight loss was 50%? Did the flame go out when the weight loss was 50%?

Eiji Yanai: The flame doesn't go away. It's not necessary that the flame goes out after 50%. It's a different oxygen index.