Mechanisms of Flame Spread over a Filter Paper Permeated with an Adhesive

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This paper presents the results of a study to elucidate the mechanisms of the flame spread over a filter paper permeated with an adhesive. For this study, two typical adhesives used for general purposes are adopted. One is polyvinyl acetate resin, and the other is urea resin. The flame spread rates and temperature profiles near leading flame edges were measured. Also, thermogravimetric analyses of the samples were performed. It was found that flame spread depends strongly on the pyrolysis reaction of the permeated adhesive. The highest pyrolysis temperature is of the pure filter paper, and the pyrolysis temperature decreases with the increase of either of permeated adhesives. Also, the flame spread rate decreases with the increase of the permeated adhesive.

The decrease of the heat flux from the gas phase to the sample surface is inferred to be a main cause to decrease the flame spread rate with the increase of the amount of the permeated polyvinyl resin. For urea resin, establishment of a residual carbon layer is inferred to be a main cause of the flame spread rate reduction. Carbon-dioxide ejection during pyrolysis reaction, which is inferred through the thermogravimetric analyses, is supposed to enhance the flame spread rate reduction.

KEYWORDS: Flame spread, Fire, Adhesive, Flame structure, Pyrolysis temperature

INTRODUCTION

Flame spread over a combustible solid surface is a basic phenomenon in a fire and a number of studies have been performed to characterize the process [1-6]. However, little is known concerning flame spread over a combustible solid which is glued to another solid by an adhesive, although various types of adhesives are widely used in furniture manufacturing and interior decoration of buildings. The development of a building fire may not be reasonably predicted without understanding of flame spread over such furniture or interior decoration.

It is easily imaginable that a solid glued by an adhesive to other solid has a complex structure, and that behavior of a flame spreading over the surface of such a solid may not be easy to explain in terms of the individual characteristics of the solid and the adhesive. This would be the reason why in few studies, the role of an adhesive on flame spread over a sample of multiple solids glued by an adhesive have been examined.

To explore the characteristics of flame spread phenomena along the surface having complex structures combined by adhesives, we have to accumulate data on flame spread over solid surfaces of simple structure. Thus, in our previous study, flame spread over a filter paper sheet permeated with an adhesive was examined experimentally [7]. To reach a systematic understanding of characteristics of the flame spread, paper sheets permeated with adhesives were prepared as fuel samples. The direction of flame spread was chosen to be downward because downward flame spread is steady and suitable for examining the basic characteristics of materials in fires. Two adhesives of different types have been used in the experimental study. One is of the main component of polyvinyl acetate resin, which is a typical thermoplastic resin, and the other is of urea resin, which is a typical thermosetting resin. Both are widely used in furniture manufacturing and interior decoration of buildings.

Throughout our previous study [7], it was shown that for both adhesives, the flame spread rate decreases with increasing amount of the permeated adhesive. The reduction of the flame spread rate was found to be much larger in the case when urea resin was permeated into the filter paper sheet compared to that in the case when polyvinyl acetate resin was permeated (Figure 1). Although these results would provide us a method for evaluating fire hazards for combined materials, we could provide a more reliable method useful for fire safety if we would have more detailed knowledge on the reason of flame spread reduction for those cases.

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Thus, a study to provide a reasonable explanation of the flame spread reduction by the permeation of an adhesive to a filter paper sheet has been performed. For understanding the phenomena concerning flame spread, the thermogravimetric characteristics of samples would be helpful, so that such experiments was conducted to examine the thermogravimetric characteristics of samples used in flame spread experiments. Also, the temperature distributions near spreading flames was measured to elucidate the heat-transfer from gas phase to the solid surface to drive the flame.
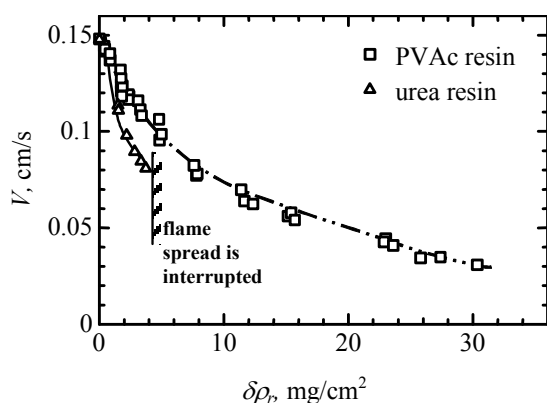

Figure 1 Flame spread rates for samples permeated with adhesives. V: flame spread rate, δ: sample thickness, ρ_r: adhesive mass permeated per unit volume.

EXPERIMENTAL

Three kinds of samples, which are the same with those used in our previous study [7], are used in the present experiments. One is of pure filter paper dried in an oven and kept in a desiccator. Its density, thickness, and mass per unit area are 0.26 g/cm^3, 0.53 mm, and 14 mg/cm^2, respectively. Others are of dried filter paper permeated with polyvinyl acetate resin and urea resin. Those samples are of surface area of 10 cm x 20 cm and prepared in the process as follows:
1) Each filter paper sheet was placed in a solution of a certain concentration of an adhesive (Polyvinyl acetate resin of 41.4 % in water or urea resin of 45.7% in water) for three minutes.
2) Then, the sheet was taken out from the solution and placed in an oven. After drying in the oven at 105 ± 2 °C for three hours, it was kept in a desiccator.
Through this process, dry filter paper sheets could be prepared by uniformly permeated with polyvinyl acetate resin or urea resin in the range of 0 to 30 mg/cm^2. The thickness of those samples was 0.53 ±

0.02 mm. The densities of samples were 0.26 g/cm^3 for dried pure filter paper and from 0.26 to 0.83 g/cm^3 for filter paper permeated with polyvinyl acetate resin or urea resin. Sheets of pure resin were also provided for comparison.

The weight of a sample in a platinum cell, whose initial value was 2.0 ~ 5.0 mg, was measured during its heating in the air from room temperature to 800 °C at a fixed temperature increasing rate. The rates of 10, 20, 30, 40, and 50 °C/min were adopted in the present experiments to examine the thermogravimetric characteristics of samples. The curve indicating the change of mass as a function of temperature or time is a TG (Thermal gravimetry) curve, and the first derivative of the TG curve is a DTG (Derivative of thermal gravimetry) curve. Both were recorded and analyzed.

The temperature variation of the gas phase over a sample sheet was measured using a set of 4 thermocouples of 1 cm interval in the direction perpendicular to the sample sheet surface. The wire diameter of the thermocouple was 50 μm and the signals from the thermocouples were recorded electrically. Just before each spread test a sample sheet was taken from the desiccator and set in a flame spread test facility, which is similar to that used in our previous studies [7, 8]. Since both sides of the sample were held by the frames, the exposed area for burning was reduced to 5 cm x 20 cm. A slit burner was used to ignite the sheet on its top edge, and behavior of the downward spreading flame was recorded using a video camera. The temperature distributions were determined on the basis of the recorded temperature variation and the flame behavior.

RESULTS AND DISCUSSION

Thermogravimetric Characteristics of Samples

The temperature increasing rate should affect pyrolysis reactions. In order to explore the characteristics of pyrolysis of a sample permeated with an adhesive, a pure dried filter paper is firstly used as a reference. The pyrolysis temperature can be inferred to be that at a peak on a DTG curve. Figure 2 shows the variation of the pyrolysis temperature with temperature increasing rate. It is seen that as the temperature increasing rate increases, the pyrolysis temperature increases and the increasing rate of pyrolysisis temperature decreases to almost zero for higher temperature increasing rates. Thus, the pyrolysis temperature at flame spreading, when the temperature increasing rate would be much higher, was assumed to be much the same as that at 50 °C/min.

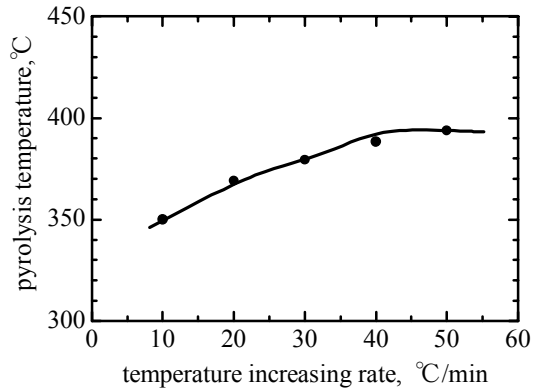Figure 3 shows the TG, DTG curves for pure filter paper, pure polyvinyl acetate resin and pure urea resin.

Figure 2 Variation of the pyrolysis temperature with temperature increasing rate.

For pure filter paper, the DTG curve has two peaks and the first peak is larger than the second one. Two peaks seems to mean that the pyrolysis reaction is composed of two stages. The main process of pyrolysis reaction is first stages and the pyrolysis temperature is 394°C.

For pure polyvinyl acetate resin, the DTG curve has three peaks. It means the pyrolysis reaction is composed of three stages. Since the first peak is largest, so the main process of pyrolysis reaction is inferred to proceed at the first stage. This is similar to the case of pure filter paper. The pyrolysis temperature is 376°C.

For pure urea resin, the DTG curve has three peaks. It means the pyrolysis reaction is composed of three stages. Since the second peak is larger than the other peaks, the main pyrolysis reaction is inferred to proceed at the second stage. The pyrolysis temperature is 331°C.
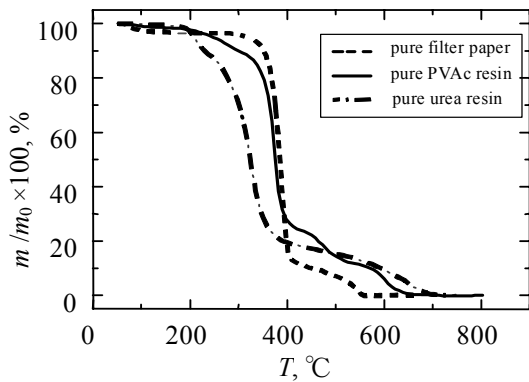

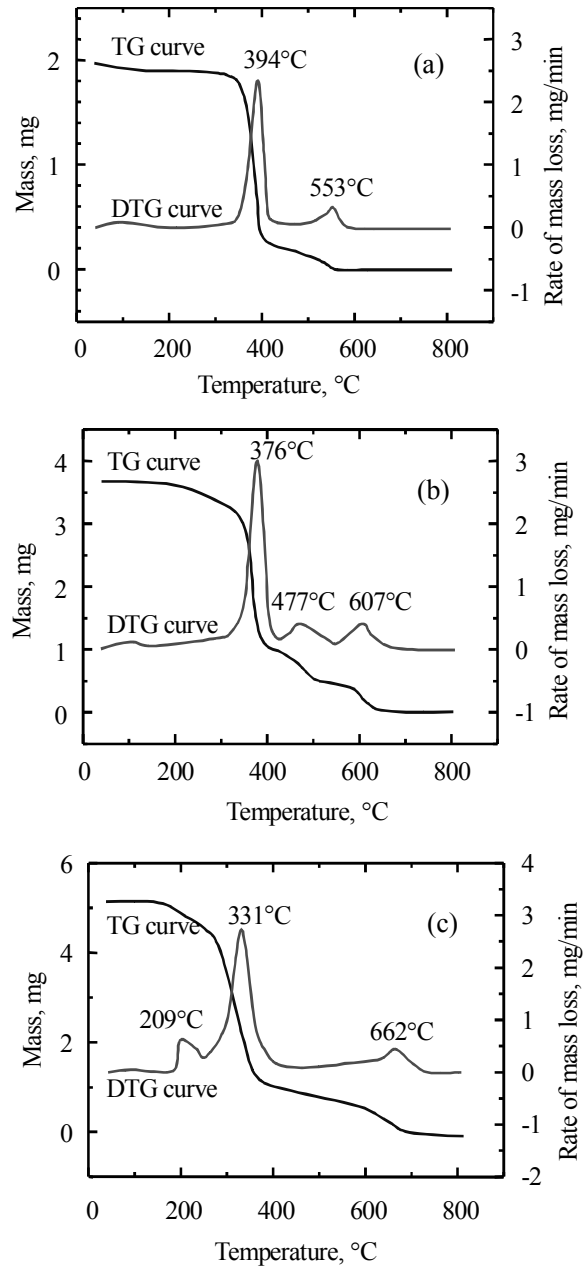Figure 4 The results of TG analysis for three kinds of samples.

Figure 3 The TG, DTG curves for (a) pure filter paper, (b) pure polyvinyl acetate resin, (c) pure urea resin.

The results of TG analysis were shown in Fgure 4. Comparing three kinds of samples, which are pure filter paper, pure polyvinyl acetate resin, and pure urea resin, the pyrolysis temperature can be found to be different. The highest is of the pure filter paper and the lowest is of the pure urea resin.

The TG curve of pure filter paper represents that about 90 % of mass is lost in the temperature range from 317 to 440 °C. At 440 °C, char remains.
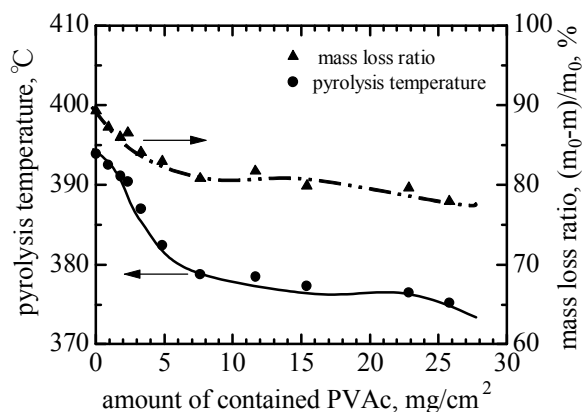
Figure 5 Variation of the pyrolysis temperature and the mass loss ratio for the filter paper permeated with the amount of polyvinyl acetate resin.

Figure 6 Variation of the pyrolysis temperature and the mass loss ratio at lower temperatures with the amount of urea resin.

Then the mass is lost further at a range of temperatures higher than 440 $^{\circ}$C and finally the sample becomes ash. It was inferred from the TG curve of a pure polyvinyl acetate resin sheet that about 75 % of mass is lost in the temperature range from 310 to 431 $^{\circ}$C. This means that the amount of remaining carbon of the polyvinyl acetate resin sheet by pyrolisis reactions is larger than that of the pure filter paper. For the case of a pure urea resin sheet, the mass starts to decrease at 200 $^{\circ}$C, and about 10 % mass is lost until 240 $^{\circ}$C. Then the rate of mass loss increases, and about 70 % mass is lost in the main process of pyrolysis reactions. In this case, the product gas at lower temperatures, when the permeated urea resin is supposed to react to generate carbon dioxide, would be carbon dioxide.

Figure 5 shows variations of the pyrolysis temperature and the mass loss ratio for the filter paper permeated with the amount of polyvinyl acetate resin. It is seen that in the range of the amounts of permeated polyvinyl acetate resin smaller than 7.6 mg/cm^2, both the pyrolysis temperature and the mass loss ratio decrease with the increase of the amount of permeated resin. On the DTG curve of a paper sheet permeated with urea resin, two peaks were observed. One is small at a lower temperature region, and the other is large at a higher temperature region. The small peak on the DTG curve represents the mass loss before main pyrolysis reaction starts and is a distinct characteristic of the pyrolysis reaction of a filter paper permeated with urea resin. Figure 6 shows variations of the pyrolysis temperature and the mass loss ratio at lower temperatures. It is seen that the pyrolysis temperature decreases with the increase of the amount of permeated urea resin. This result is similar to that of the filter paper permeated with various amounts of polyvinyl acetate resin. It
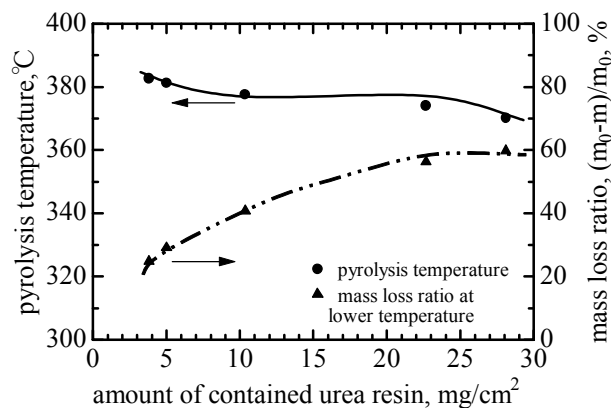
should be noted that the mass loss ratio at a lower temperature region, inferred to indicate carbon dioxide generation, increases with the amount of permeated urea resin.

It can be realized through the thermogravimetric analyses that flame spread depends strongly on the pyrolysis reaction of the permeated adhesive.

Temperature Distributions near Leading Flame Edges

Figure 7 shows temperature distributions near the leading flame edges spreading over a pure filter paper sheet, polyvinyl acetate resin permeated one, and urea resin permeated one. It is seen that the distance from a higher temperature zone to the surface is largest for the pure filter paper and shortest for urea resin permeated one. The temperature at the surface is lowest for the pure filter paper and highest for the urea resin permeated one. These results are not inconsistent with the results of thermogravimetric analyses and similar to those of flame spread experiments by Hirano et al. [9]. Near the limit of flame spread the surface temperature is higher than that at stable flame spread. In this study, the flame spread over a pure filter paper sheet is more stable than those over other two adhesive permeated sheets, and that over a urea resin permeated filter paper sheet is the most unstable.

Heat Transfer and Retardation Mechanisms of Flame Spread

In discussion on the mechanisms of flame spread, it is important to explore the process of heat transfer to the not-yet burning part of the sample sheet. In
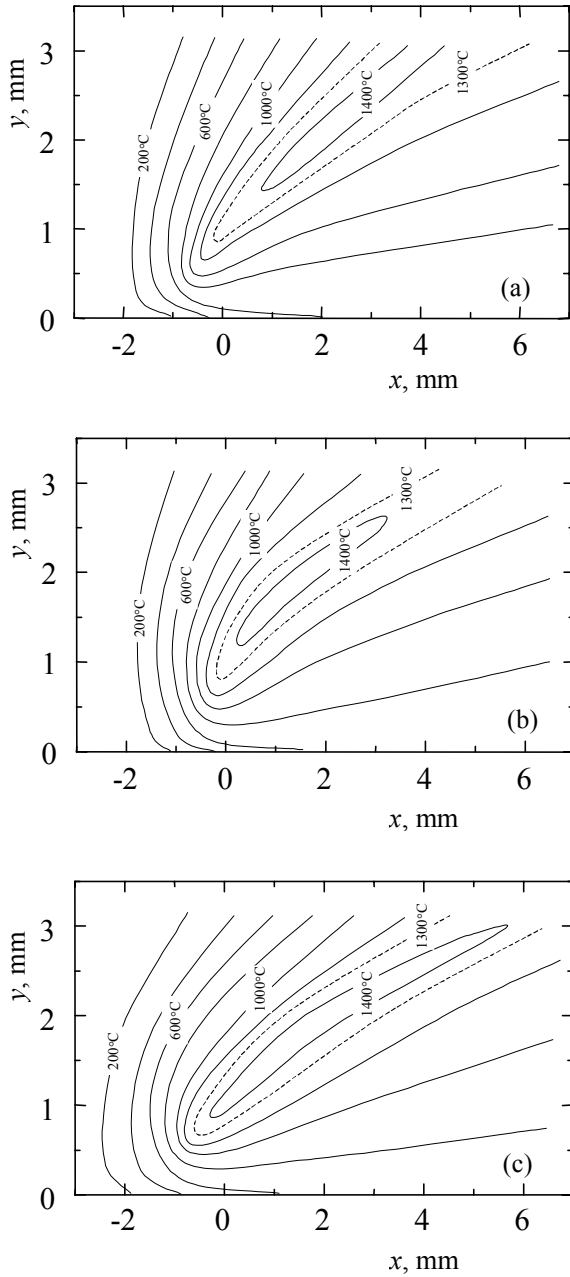
Figure 7 Temperature distributions near the leading flame edges spreading over (a) a pure filter paper, (b) polyvinyl acetate resin permeated filter paper, and (c) urea resin permeated filter paper.

x : distance from the leading flame edge

y : distance from the test piece surface

previous studies on flame spread [1-6], various equations have been derived to predict the flame spread rate on the basis of heat transfer consideration. The following is one of such equations [5]:

$$V\delta\rho = \frac{\delta}{c\int_{-\delta/2}^{\delta/2}\left(T_{x=0} - T_r\right)dy}\left\{2\int_{-\infty}^{0}\left(\lambda_g\frac{\partial T}{\partial y}\right)_w dx\right.$$

$$\left. -2\int_{-\infty}^{0}\varepsilon\sigma\left(T_w^4 - T_r^4\right)dx + \int_{-\delta/2}^{\delta/2}\left(\lambda_s\frac{\partial T}{\partial x}\right)_{x=0} dy\right\}, \quad (1)$$

where ρ and c are the density and specific heat of the sample, respectively. T is the temperature and λ_g and λ_s are thermal conductivities of the gas and solid, respectively. The coordinates are shown in Figure 8, and suffixes, x=0, r, and w for T refer to the leading edge of the pyrolysis zone, room, and sheet surface respectively.

The first, second, and third terms in the braces of the right hand side of Eq. (1) represent the heat flux Q_I from the gas phase to the sheet surfaces of both sides, radiation heat loss Q_{II} from the sheet surfaces to ambient, and heat flux Q_{III} through solid phase in the direction of flame spread, respectively. Equation (1) can be rewritten as

$$V\delta\rho = A\left(Q_I + Q_{II} + Q_{III}\right) \quad (2)$$

where

$$A = \frac{\delta}{c\int_{-\delta/2}^{\delta/2}\left(T_{x=0} - T_r\right)dy} \quad (3)$$

A is the effective factor for temperature increase by heating, and for discussion on flame spread the values of AQ_I, AQ_{II}, and AQ_{III} are more convenient than those of Q_I, Q_{II}, and Q_{III} .
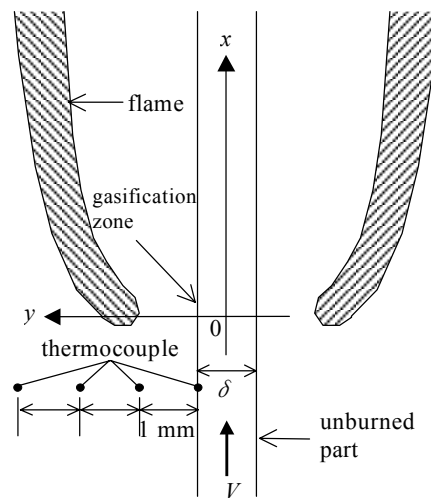

Figure 8 Coordinates for discussion on retardation mechanisms of flame spread.

Figure 9 Heat transferred to the solid in various modes and mass burning rate in the cases of flame spread over filter paper sheets permeated with various amounts of polyvinyl acetate resin.
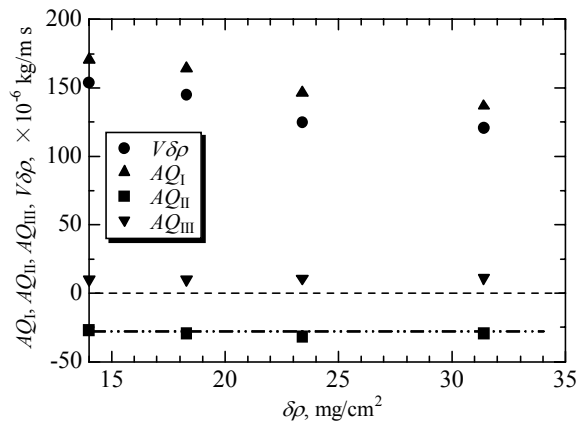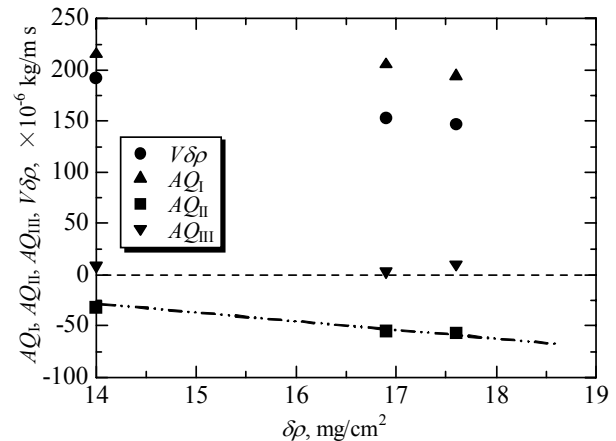
Figure 10 Heat transferred to the solid in various modes and mass burning rate in the cases of flame spread over filter paper sheets permeated with various amounts of urea resin.

On the basis of the results of temperature measurements, AQ_I, AQ_{II}, and AQ_{III} are evaluated. Figures 9 and 10 show the results of the evaluation. The left hand side $V\delta\rho$ of Equation (1) represents the mass burning rate per unit width of the sheet, and can be estimated on the basis of the results of flame spread experiments. $V\delta\rho$ are also presented in Figures 9 and 10. The values of AQ_{II} and AQ_{III} for polyvinyl acetate resin permeated filter paper are not so different from those for pure filter paper. This fact means that the cause of spread rate retardation is attributable to the reduction of heat flux from the gas phase to the sheet surface. AQ_{III} for polyvinyl acetate resin permeated filter paper is almost the same with that for pure filter paper, while AQ_{II} for urea resin permeated filter paper is larger than that for pure filter paper. This fact means that the cause of retardation is attributable not only to the reduction of heat flux from gas phase to the sheet surface but also to the increase of radiation loss.

As mentioned previously, the pyrolysis temperature is shown to decrease with increase of the amount of permeated resin. Since specific heats of paper and resin as well as the thickness of the sample are almost the same, the decrease of pyrolysis temperature should result in the increases of A. If Q_I, is constant, and Q_{II}, and Q_{III} can be neglected as assumed in previous studies [1-6], then $V\delta\rho$ should increase with the decrease of pyrolysis temperature. However, the results of previous flame spread experiments indicate that the mass burning rate decreases with the decrease of pyrolysis temperature caused by the increase of the amount of permeated resin [7]. According to the results, the first term in

the braces should decrease with the increase of the amount of permeated resin. This coincides with the results of temperature measurements (Figure 7).

The results of the present thermogravimetric analyses indicate that residue, the main component of which would be carbon, increases with the amount of permeated resin. This means that the thickness of a layer composed of residue established over the sample surface increases with the increase of the amount of permeated resin. The residue layer would be effective to reduce the heat flux from the gas phase. The reduction of combustible gas to the gas phase would be the cause to approach the leading flame edge to the surface. These are the reasons why the flame spread rate decreases and the higher temperature region approaches to the sample surface with the increase of the permeated resin.

In the case of the sample permeated with urea resin, the amount of residue is larger than that of pure filter paper or that of filter paper permeated with polyvinyl acetate resin. Also, the results of thermogravimetric experiments indicate that carbon dioxide would be ejected to the gas phase by pyrolysis reaction at a lower temperature. This carbon dioxide ejection near the leading flame edge is also inferred to be effective to reduce the flame spread.

CONCLUSIONS

A study has been performed to elucidate the mechanisms of flame spread over filter papers permeated with an adhesive by flame spread

experiments, thernogravimetric analyses, and temperature measurements. As the results, the following conclusions are derived:

1. Flame spread depends strongly on the pyrolysis reaction of a permeated adhesive. The highest pyrolysis temperature is of the pure filter paper, and the pyrolysis temperature decreases with the increase of the amount of permeated resin. However, the flame spread rate decreases with the increase of the amount of permeated resin. This means that the heat flux from the gas phase to the sample sheet surface decreases with the increase of the amount of permeated resin.

2. The decrease of the heat flux to the sample surface with the increase of the permeated resin is inferred to be the main cause to decrease the flame spread rate over a filter paper permeated with polyvinyl acetate resin permeation. For polyvinyl acetate resin, the residue after pyrolysis reaction forms a layer to reduce the heat flux to the sample surface.

3. For urea resin, also the residue forms a layer over the sample sheet surface. Also, the results of thermogravimetric analyses indicate that carbon dioxide would ejected to the gas phase beneath the leading flame edge. Thus, the reduction of flame spread over a filter paper permeated with urea resin is inferred to be not only due to residue carbon layer formed on the surface but also due to carbon dioxide ejected to the gas phase.

REFERENCES

1. Friedman, R. A., "A Survey of Knowledge about Idealized Fire Spread over Surfaces", Fire Res. Abs. Rev., 10:1, 1-8, 1968.

2. Williams, F. A., "Mechanisms of Fire Spread", Proc. Comb. Inst. 16, 1281-1294, 1976.

3. Fernandez-Pello, A. C. and Hirano, T., "Controlling Mechanisms of Flame Spread", Combust. Sci. Technol., 32:1, 1-31, 1983.

4. Di Blassi, C., "Modeling and Simulation of Combustion Processes of Charing and Non-Charing Solid Fuels", Prog. Energy Combust. Sci., 19:1, 71-104, 1993.

5. Hirano, T. "Flame Spread", in Fire Sci. Technol., Proc. Fifth Asia-Oceania Symp., eds. M.A. Delichatsios, B. Z. Dlugogorski, and E. M. Kennedy, pp. 40-54, Univ. Newcastle, Newcastle, 2001.

6. Delichatsios, M. A., Altenkirch, R. A., Bundy, M. F., Bhattacharajee, S., Tang, L., and Sacksteder, K., "Creeping Flame Spread Along Fuel Cylinders in Forced and Natural Flows and Microgravity", Proc. Combust. Inst. 28, 2835-2842, 2000.

7. Gao, L., Dobashi, R., and Hirano, T., "Flame Spread over a Cellulose Sheet Permeated with an Adhesive", in Fire Safety Science, Proc. Fifth Int. Symp. ed. Y. Hasemi, pp. 357-366, Int. Assoc. Fire Safety Sci., London, 1997.

8. Hirano, T., Noreikis, S. E., and Waterman, T. E., "Postulation of Flame Spread Mechanisms", Combust. Flame, 22:3, 353-363, 1974.

9. Hirano, T., Sato, K., and Tazawa, K., "Instability of Downward Flame Spread over Paper in an Air Stream", Combust. Flame, 26:2, 191-200, 1976.